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THE ATTEMPTED SYNTHESIS OF TETRAPHENYLENE BY ULLMANN REACTIONS

A THESIS

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THE ATTEMPTED SYNTHESIS OF

TETRAPHENYLENE BY ULLMANN REACTIONS

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TABLE OF CONTENTS

Page

LIST OF ILLUSTRATIONS

SUMMARY

The purpose of this research project was to attempt the synthesis of tetraphenylene by means of the Ullmann reaction. The only reported synthesis of this molecule is the reaction of the Grignard reagent of 2,2'-dibromobiphenyl with cupric chloride. No other preparation is known and little is known about the chemistry of tetraphenylene. If tetraphenylene could be synthesized by the Ullmann reaction, it would present a method of preparing derivatives of tetraphenylene.

The first approach to the preparation of this compound was to learn if it could be formed by an Ullmann reaction of 2,2'-diiodobiphenyl or 2,2'-biphenyleneiodonium iodide. These compounds were prepared starting with 2-nitrochlorobenzene. This reacted with copper powder to give 2,2'-dinitrobiphenyl, after which the 2,2'-dinitrobiphenyl was reduced to 2,2'-diaminobiphenyl. The diazotization of the amine and subsequent treatment with potassium iodide yielded both 2,2'-diiodobiphenyl and 2,2'-biphenyleneiodonium iodide. The heating of these compounds with copper powder failed to produce any discernable tetraphenylene.

2,2'-Biphenyleneiodonium iodide, which was washed with sodium thiosulfate solution, produced biphenylene sulfide when it was heated with copper powder.

The other approach to tetraphenylene was a series of reactions involving single couplings of substituted biphenyls. 2'-Nitro-2-aminobiphenyl was prepared by the reduction of 2,2'-dinitrobiphenyl with sodium polysulfide. The nitroamine was made also by the reaction of

of sodium hypobromite upon 2'-nitro-2-carboxamidobiphenyl, which was heretofore an unreported compound. 2'-Nitro-2-iodobiphenyl was prepared by the diazotization and subsequent Sandmeyer reaction of 2'-nitro-2-aminobiphenyl. This reaction gave low yields of the desired product, and for the most part gave a black solid of unknown composition. Some reports in the literature indicated that this black solid was at least in part biphenyleneiodonium iodide; however, in this research a sample of the black solid was found to contain nitrogen but no halogen. The reaction of 2'-nitro-2-iodobiphenyl with copper powder was tried using dimethylformamide and nitrobenzene as solvents, but no 2,2'-di(2-nitrophenyl)biphenyl was formed. However, this compound was prepared by heating 2'-nitro-2-iodobiphenyl with copper. The overall yield of 2,2'-di(2-nitrophenyl)biphenyl, based on the starting material, 2-nitrochlorobenzene, was about 1.2 per cent.

An attempt at an alternate approach to the tetraphenylene system involving the preparation of 2'-iodo-2-carboxybiphenyl was tried, but the yield of this compound was too low to be practical. 2,2'-Di(2-nitrophenyl)biphenyl was reduced to 2,2'-di(2-aminophenyl)biphenyl with hydrogen and platinum. The yields of this reaction were low. With semimicro techniques the preparation of 2,2'-di(2-iodophenyl)biphenyl was attempted by the diazotization and subsequent Sandmeyer reaction of 2,2'-di(2-aminophenyl)biphenyl. From this reaction a few milligrams of 2'-phenyl-2-(2-iodophenyl)biphenyl was obtained. Before the identity of this compound was established, it was reacted with copper powder to give only a trace of a compound which may be ortho-octaphenyl.

CHAPTER I

INTRODUCTION

Tetraphenylene is a large organic molecule with the structure illustrated in Fig. 1.

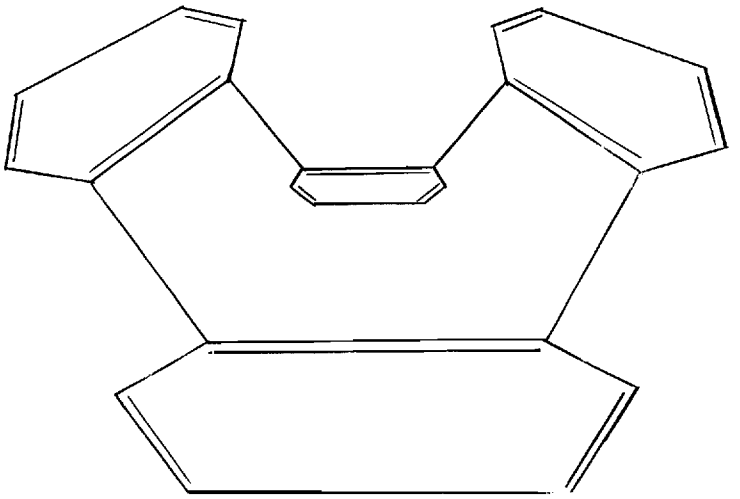

Figure 1. Tetraphenylene

Tetraphenylene is of theoretical interest because of its cycloocta-tetraene ring, which is postulated to be in the more stable "boat form" by Karle and Brockway (10), who made x-ray diffraction studies on the compound.

The history of the preparation of tetraphenylene is very brief. Its preparation was first reported in 1928 by Sircar and Majumdar (24), who obtained white plates melting at 304-305°C. from the reaction of

4,4'-diiodobiphenyl with copper powder and claimed that these plates were tetraphenylene. Their results could not be duplicated in 1929 by Kuhn (13), who reported that the reaction of 4,4'-diiodobiphenyl with Nature-kupfer C yielded para-quarterphenyl, biphenyl, and an iodine containing compound.

Rapson and Shuttleworth (20) in 1943 reported the preparation of tetraphenylene melting at 233°C. in 16 per cent yield from the reaction of the Grignard reagent of 2,2'-dibromobiphenyl with cupric chloride.

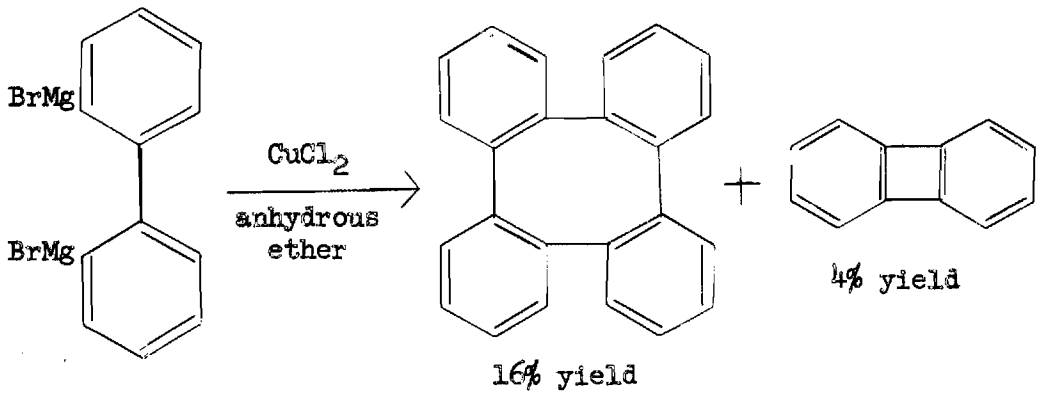

Figure 2. Rapson and Shuttleworth's
Preparation of Tetraphenylene

Rapson and Shuttleworth made a bromo derivative and a tetranitro derivative from tetraphenylene. They also prepared 1,2,3,4,5,6-tribenz-1,3,5,7-cyclooctatetraene by the oxidation of tetraphenylene and the subsequent decarboxylation of the oxidation product (23). Since this report there has been no further study of the chemistry of tetraphenylene. However,

since then Karle and Brockway (10) made their x-ray diffraction studies on tetraphenylene.

This research was undertaken to determine whether tetraphenylene could be prepared satisfactorily by the Ullmann reaction. Some substituents which interfere with the Grignard reaction augment the Ullmann reaction; this would make it possible to prepare derivatives of tetraphenylene.

The Ullmann reaction has been used in many cases to join aromatic rings (6). In one case, a preparation of biphenylene, a variation of the Ullmann reaction used in preparing biphenylene employed cuprous oxide instead of copper was used to effect a double coupling, a reaction in which two molecules join at two points.

Some of the intermediate compounds considered for the synthesis of tetraphenylene, namely the biphenyls, were reported in the literature, but the ortho-tetraphenyls, also considered intermediates, were unreported. The research was begun and continued with the preparation of many of these compounds.

CHAPTER II

DISCUSSION

The most direct approach for synthesizing tetraphenylene by means of the Ullmann reaction would be a coupling reaction which would give tetraphenylene as an immediate product. Suggested compounds for this type of reaction are ortho-diiodobenzene, 2,2'-diiodobiphenyl, and 2,2'-biphenyleneiodonium iodide. A reaction using ortho-diiodobenzene would not be a good choice because of the possibility of a number of intermediate products. According to Fanta (6) no one has reported an Ullmann reaction using ortho-diiodobenzene as the only halogen compound.

The approach involving 2,2'-diiodobiphenyl and 2,2'-biphenyleneiodonium iodide.--Even though Lothrop (15) reported that the reaction of 2,2'-biphenyleneiodonium iodide with cuprous oxide gave biphenylene as a product, the approach with 2,2'-diiodobiphenyl and 2,2'-biphenyleneiodonium iodide was tried. 2-Chloronitrobenzene, an Eastman white label product, was used as the starting material for this approach since no appropriate 2,2'-disubstituted biphenyl was available. 2-Chloronitrobenzene was known to react with copper powder to form 2,2'-dinitrobiphenyl (7). This reaction was tried using sand as diluent, and the yield obtained in this reaction was about 40 per cent compared to the reported 50-60 per cent given in the original reference. Le Fevre (14) reported that this reaction could be run without any sand with no decrease in yield. This method was also tried but only a 33 per cent yield resulted.

Kornblum (12) reported the use of dimethylformamide as a solvent for this and other Ullmann reactions giving higher yields than when this solvent

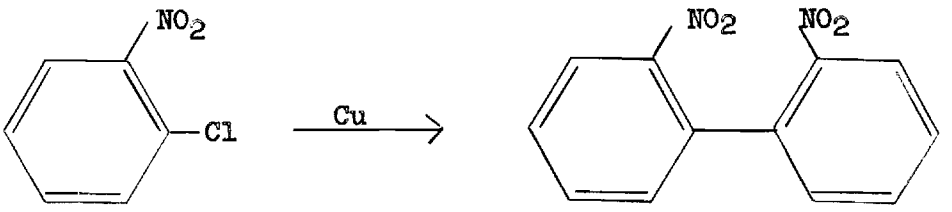

Figure 3. The Preparation of 2,2'-Dinitrobiphenyl

is not used. He also recommended a type of copper powder, designated as 44F, for the Ullmann reaction. Many reactions were run with a procedure similar to that of Kornblum. The yields at first approached the 80 per cent yield reported by Kornblum, but as the 44F copper powder aged, the yields of this reaction decreased. A new supply of 44F copper powder gave better yields than aged 44F copper powder, but they were not as good as those which were obtained initially with the original copper powder. Kornblum's procedure was used to prepare the bulk of the 2,2'-dinitrobiphenyl satisfactorily employed. This material was in the form of yellow needle-like crystals and melted at 124-125°C.

The next reaction was the reduction of the nitro groups of 2,2'-dinitrobiphenyl thus preparing 2,2'-diaminobiphenyl. A preparation of this compound was described by Mascarelli, Gatti, and Pirona (16) who reduced 2,2'-dinitrobiphenyl with ammonium sulfide to 2'-nitro-2-aminobiphenyl which was described as a yellow oil. Without further purification of the oil it was reduced with tin and hydrochloric acid to

2,2'-diaminobiphenyl, reported to melt at 81°C. The diaminobiphenyl was also prepared by Lothrop (15) who employed tin and hydrochloric

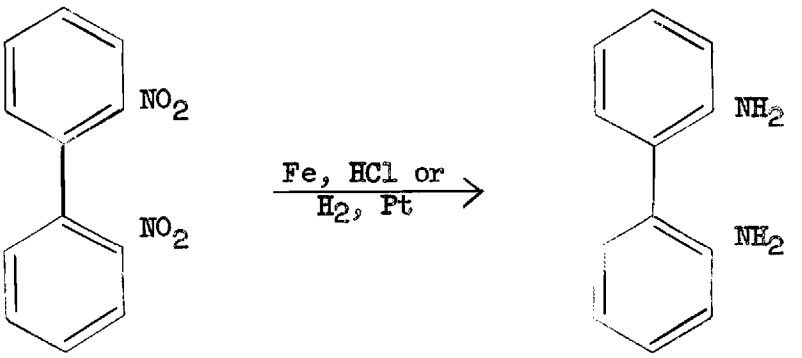

Figure 4. The Preparation of 2,2'-Diaminobiphenyl

acid to reduce both nitro groups in one step.

This reaction was tried at first with iron filings and hydrochloric acid as the reducing agent. The reaction product was difficult to extract because of the iron sludge. The product, gray-brown crystals melting at 78-80°C., was obtained in a 30 per cent yield.

This reaction was repeated with hydrogen and platinum oxide catalyst and benzene as a solvent. Yields of 2,2'-diaminobiphenyl ranged from 71 to 89 per cent. The product was white crystals melting at 78-80°C.

The preparation of 2,2'-diiodobiphenyl and 2,2'-biphenyleneiodonium iodide by the diazotization of 2,2'-diaminobiphenyl and the subsequent Sandmeyer reaction has been reported by Lothrop (15) who described 2,2'-diiodobiphenyl as a white crystalline solid melting at 106-108°C. and 2,2'-biphenyleneiodonium iodide as a yellow-green solid melting with decomposition between 205-210°C.

This reaction was tried by diazotizing 2,2'-diaminobiphenyl in the usual manner with hydrochloric acid and sodium nitrite in a cold

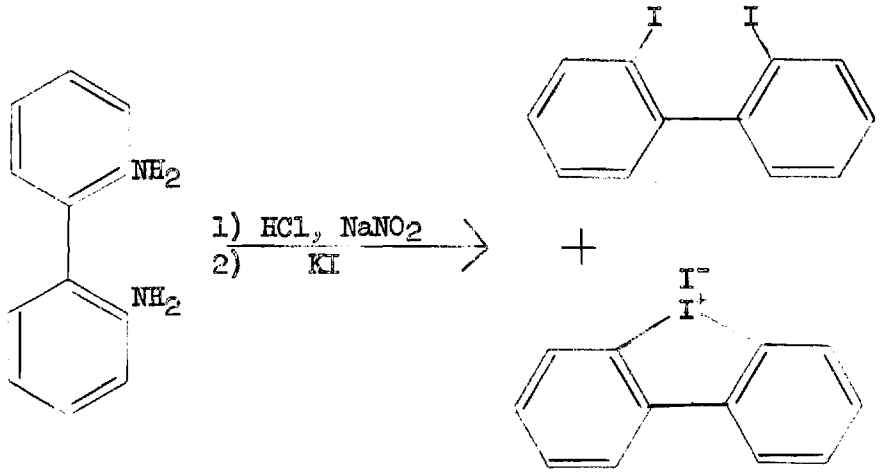

Figure 5. The Preparation of 2,2'-Diiodobiphenyl and 2,2'-Biphenyleneiodonium Iodide

solution. When potassium iodide solution was added to the diazonium salt solution or even when the addition was reversed, a black foamy mass appeared. During the first preparation this black mass was washed with a sodium thiosulfate solution, but in the later preparation this was omitted because of an effect which is discussed later (see below, p. 9). After this washing, if it was done, the black solid was washed with an excess of acetone. A little material dissolved and the color of the solid was lightened. The acetone wash was concentrated to give a gray solid which, upon recrystallization from ethanol, yielded white needles melting at 109°C. These were taken to be 2,2'-diiodobiphenyl. A small amount of the dark solid dissolved in water; this water upon cooling gave a yellow solid melting at 203-206°C. No further

attempt was made to purify the dark solid, which was taken to be 2,2'-biphenyleneiodonium iodide.

The coupling reactions of 2,2'-diiodobiphenyl and 2,2'-biphenyleneiodonium iodide was tried. 2,2'-Biphenyleneiodonium iodide was heated with treated Baker's copper powder, a small amount of material, melting at 109-110°C., sublimed from the reaction. The material was taken to biphenylene because its melting point and a red picrate agreed with the results of Lothrop (15), who reported that the same reaction gave biphenylene. He postulated that the formation of biphenylene was due to cuprous oxide impurities in the copper. 2,2'-Biphenyleneiodonium iodide, which had been washed with sodium thiosulfate, was heated with treated 44F copper powder in dimethylformamide, at reflux. The reaction

I II

Figure 6. Biphenylene(I) and Biphenylene Sulfide(II)

product was washed with ethanol, and after several recrystallizations from ethanol, a product, labeled SDL I, melting at 98.0-98.5°C. was obtained. The experimental data of SDL I compared quite similarly with the known information about biphenylene sulfide, hence it was concluded that they were the same compound. The sulfur in the biphenylene sulfide may have come from the sodium thiosulfate which was used in

solution to wash the biphenyleneiodonium iodide. This reaction was repeated, but the sodium thiosulfate wash was omitted, and a white solid containing iodine was the product. After several recrystallizations this compound had a melting point of 104-105°C. which is a few degrees low for the melting point of 2,2'-diiodobiphenyl. 2,2'-Diiodobiphenyl in dimethylformamide solution was heated with treated 44F copper powder; after the product was extracted with and recrystallized from ethanol, gray-white crystals melting at 109°C. were obtained. These were the starting material, 2,2'-diiodobiphenyl.

The results of the above reactions and the work of Lothrop indicate that the approach to tetraphenylene by means of a double coupling reaction which is unlikely to occur to an extent which would give a noticeable yield.

The approach involving single coupling reactions.--Another approach to tetraphenylene was to effect reactions involving single couplings. An approach of this type would be to couple 2'-nitro-2-iodobiphenyl in an Ullmann reaction. Then one could convert the nitro groups to iodo groups by a series of reactions and next attempt an internal Ullmann coupling. This approach with some variations was tried.

2'-Nitro-2-iodobiphenyl, as previously mentioned, is a compound upon which one could try this approach. Mascarelli et al. (6) prepared this compound from an oil which, they said, was 2'-nitro-2-aminobiphenyl. They prepared the oil by the reduction of 2,2'-dinitrobiphenyl with ammonium sulfide. Purdie (19) gave a preparation of 2'-nitro-2-amino-biphenyl by the reduction of 2,2'-dinitrobiphenyl with sodium polysulfide. He describes the amine as an orange crystalline solid melting at 95-96°C.

Purdie's procedure for preparing 2'-nitro-2-aminobiphenyl was tried because a definite product was reported and because the reducing agent, sodium polysulfide, was easier to handle than hydrogen sulfide gas. Purdie in his procedure did not indicate whether his weight of sodium sulfide sulfide included water of hydration. The reaction was tried with the weight given as the weight of anhydrous sodium sulfide. This reaction produced, for the most part, yellow crystals melting at 137.0-137.5°C. This product was identified as diphenazomonoxide from an analysis for the elements and the melting point. Ullmann and Dieterle (25) had also reported that this compound was obtained as the product

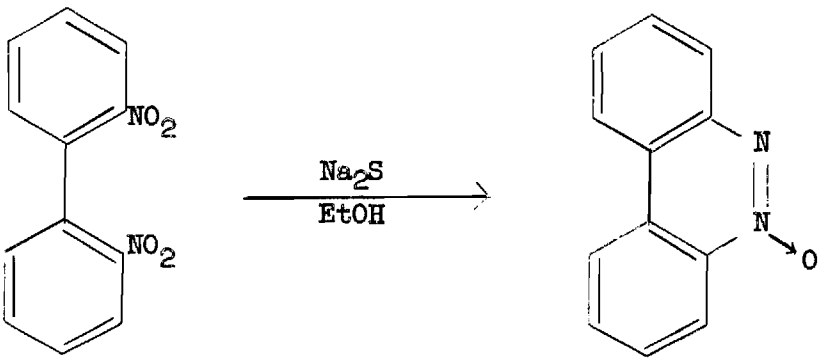

Figure 7. The Preparation of Diphenazonmonoxide

when 2,2'-dinitrobiphenyl was reduced with sodium sulfide in ethanol. The preparation of 2'-nitro-2-aminobiphenyl was repeated with the weight of the sodium sulfide given by Purdie being taken as the weight of sodium sulfide nonahydrate. This reaction produced, instead of the product described by Purdie, a red-orange oil which resisted crystallization from ethanol and other common solvents. This oil, however, was

basic as evidenced by solubility in hydrochloric acid solutions. When concentrated hydrochloric acid was added to the red oil, a light yellow solid was formed. This solid was moderately soluble in water. It was assumed to be the impure hydrochloride of 2'-nitro-2-aminobiphenyl. When this solid was subjected to the conditions of a diazotization and subsequent Sandmeyer reaction, a small amount of material resembling 2'-nitro-2-iodobiphenyl was obtained (see below p. 42).

Since 2'-nitro-2-iodobiphenyl could only be made in small quantities from the oil of Purdie's procedure, an alternate preparation of 2'-nitro-2-aminobiphenyl was investigated. This was tried by means of a Hoffmann reaction upon 2'-nitro-2-carboxamidobiphenyl. This compound was synthesized starting with 2-nitroaniline and 2-bromotoluene. The 2-nitroaniline gave 2-nitroiodobenzene in 80 per cent yield by means of a diazotization and Sandmeyer reaction. The 2-bromotoluene was oxidized with potassium permanganate to 2-bromobenzoic acid in 58 per cent yield. This acid was esterified with anhydrous methanol and hydrogen chloride to give methyl 2-bromobenzoate in 87 per cent yield. The reaction of 2-nitroiodobenzene and methyl 2-bromobenzoate with copper powder was described by Sadler and Powell (21) and was mentioned by Shuttleworth and Rapson (23). With a one to one mole ratio of 2-nitroiodobenzene to methyl 2-bromobenzoate, Sadler and Powell obtained a 22 per cent yield of 2'-nitro-2-carboxybiphenyl which melted at 165-165.5°C. With a 1.6 to 1.0 ratio, Shuttleworth and Rapson reported a 68 per cent yield. This reaction was tried with the 1.6 to 1.0 ratio. The reactants were heated with 44F copper powder in the 250-270°C. range, and the products were hydrolyzed with potassium hydroxide. A 26.7 per cent yield of 2'-nitro-2-carboxybiphenyl melting at 165-166°C. was obtained.

2'-Nitro-2-carboxybiphenyl was reacted first with thionyl chloride and next with ammonium hydroxide to give, in 80 per cent yield, the

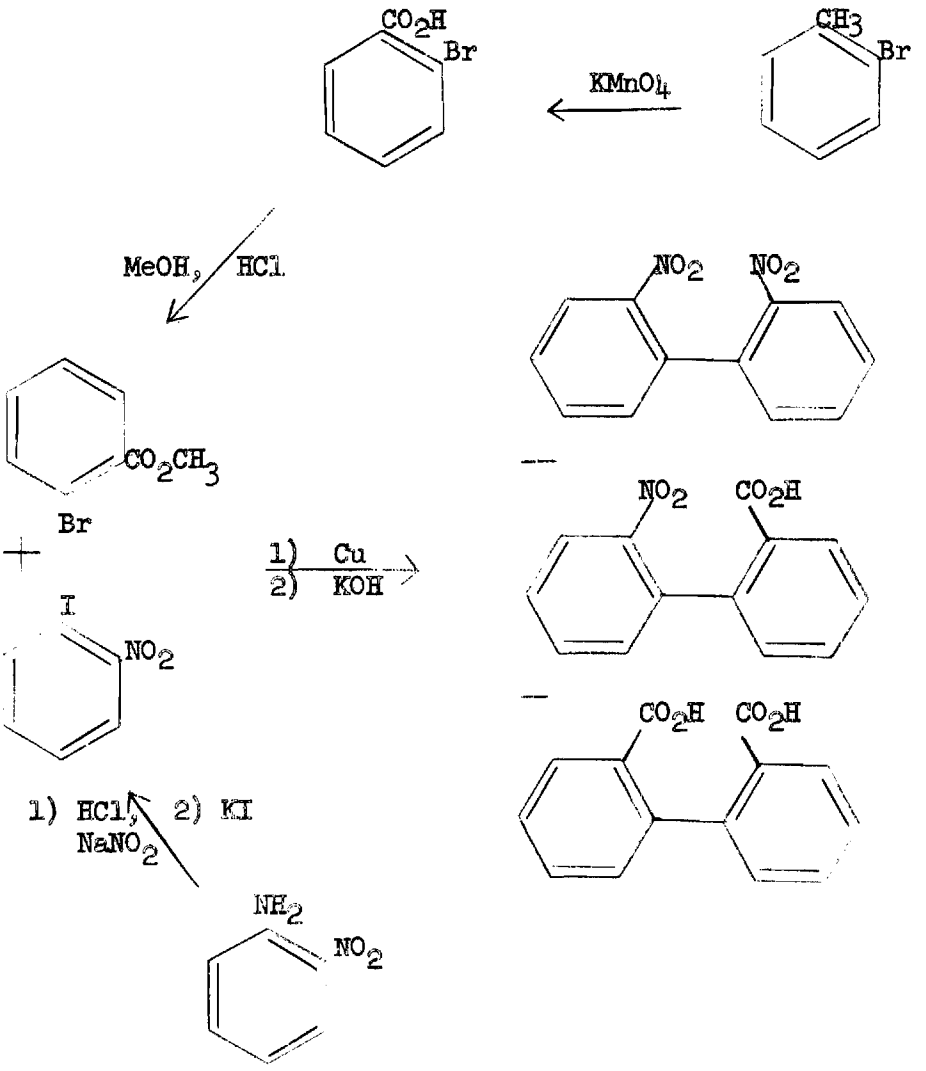

Figure 8. The Synthesis of 2'-Nitro-2-carboxybiphenyl

2'-nitro-2-carboxamidobiphenyl which melted at 136.5-137.5°C. This compound has not been reported in the literature. Upon reaction with sodium hypobromite solution the 2'-nitro-2-carboxamidobiphenyl yielded a red oil. Attempts to crystallize this oil were unsuccessful.

However, it did dissolve in hydrochloric acid solution, and after the solution was made basic with ammonium hydroxide and was allowed to stand, yellow crystals melting at 62-65°C. were obtained. An acetyl derivative

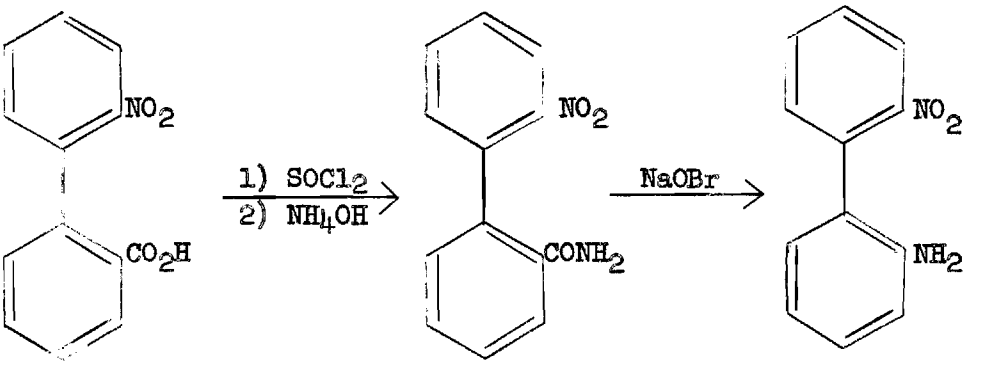

Figure 9. The Alternate Preparation of 2'-Nitro-2-aminobiphenyl

of these crystals melted at 157-158°C., which is in agreement with the melting point of the acetamide of 2'-nitro-2-aminobiphenyl as reported by Purdie. A more recent report by Fairfull *et al.* (5) gave the melting point of 2'-nitro-2-aminobiphenyl as 64-65°C. This contradicted the melting point of 95-96°C. reported by Purdie (19).

It was speculated that if the red oil from the above Hoffmann reaction could give a solid product by being dissolved in hydrochloric acid and being precipitated with ammonium hydroxide, perhaps the red oil, obtained from the reduction of 2,2'-dinitrobiphenyl, would give similar results. This was tried and a yellow solid melting at 63-65°C. was obtained. This solid was 2'-nitro-2-aminobiphenyl, and was obtained in yields of 40-50 per cent.

The next step in this single coupling approach was to prepare 2'-nitro-2-iodobiphenyl from the 2'-nitro-2-aminobiphenyl. Mascarelli

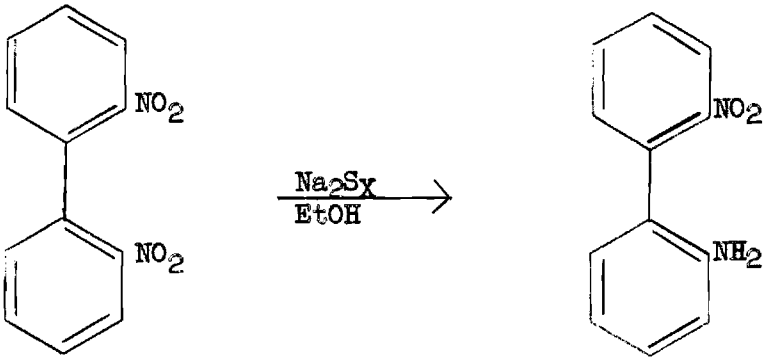

Figure 10. The Preparation of 2'-Nitro-2-aminobiphenyl

et al. (16) performed a diazotization and a Sandmeyer reaction upon a sample of 2'-nitro-2-aminobiphenyl which they had described as a yellow oil. During the Sandmeyer reaction they reported the formation of a black solid which was extracted with ether to give the yellow product 2'-nitro-2-iodobiphenyl which melted at 81-80°C. They did not report the per cent yield or the identification of any other products. In a later publication, however, Mascarelli et al. (17) reported that biphenyleneiodonium iodide was formed in this reaction.

The diazotization and Sandmeyer reaction of 2'-nitro-2-amino-biphenyl was tried with many variations, but most of the results were the same. After the addition of the potassium iodide solution to the diazonium salt solution or vice versa, a black foamy mass appeared. When the reaction had settled, this material appeared as a sticky solid. From this black solid some 2'-nitro-2-iodobiphenyl melting at

81-82°C. could be obtained. One way by which this was effected was to extract the black solid with cyclohexane which dissolved the 2'-nitro-2-iodobiphenyl. Another method was to add ether which dissolved most of the black solid, and then extract the ether solution with sodium hydroxide. The ether was dried over potassium hydroxide pellets (1). The bases removed much dark material from the ether solution and the desired product, 2'-nitro-2-iodobiphenyl, was left in the solution.

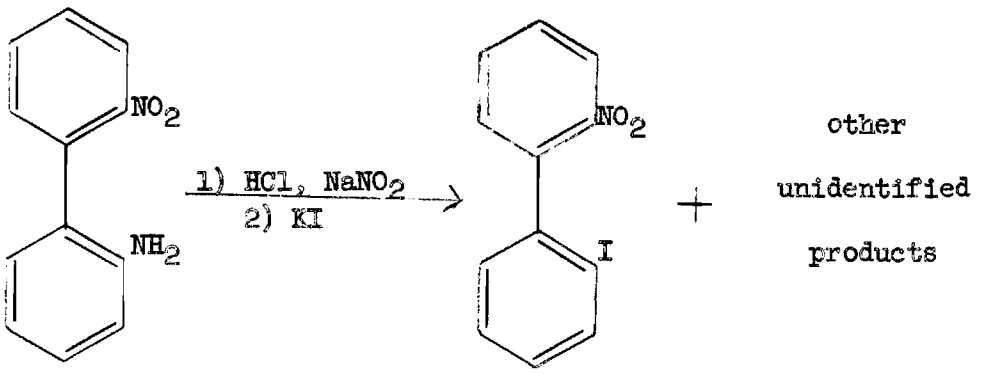

Figure 11. The Preparation of 2'-Nitro-2-iodobiphenyl

Mascarelli et al. (17) reported that ether insoluble biphenyleneiodonium iodide was formed when certain 2,2'-disubstituted biphenyls were subjected to the Sandmeyer reaction. They also reported that no carbazole, a nitrogen-containing cyclic compound, was formed by the Sandmeyer reaction of 2'-nitro-2-aminobiphenyl. However, during the present research little ether insoluble product was obtained from the reaction of the diazonium ion of 2'-nitro-2-aminobiphenyl with potassium iodide. After the product of this reaction had been extracted with cyclohexane, it was found to contain nitrogen and no halogen. This indicated that little biphenyleneiodonium iodide was formed.

During one attempted preparation of 2'-nitro-2-iodobiphenyl, potassium iodide solution was added to a neutral solution of the diazonium salt of 2'-nitro-2-aminobiphenyl. This produced a maroon precipitate which exploded on standing. This explosive material, which sometimes occurred in more acid solutions, might have been the diazonium iodide because it formed on the addition of the iodide ion and most diazonium salts are known to be explosive.

When the diazotization and Sandmeyer reactions of 2'-nitro-2-aminobiphenyl were carried out in an acetic acid solution, only a small amount of 2'-nitro-2-iodobiphenyl was obtained. In another preparation the diazonium tetrafluoroborate salt of 2'-nitro-2-aminobiphenyl was isolated in 71 per cent yield, but in making the 2'-nitro-2-iodobiphenyl from this salt only a 13.5 per cent yield based on the amine was obtained. This indicated that the low yield of 2'-nitro-2-iodobiphenyl is not due to the lack of the diazotization of 2'-nitro-2-aminobiphenyl.

The method of preparing 2'-nitro-2-iodobiphenyl involving the previously mentioned cyclohexane extraction gave the product in close to 10 per cent yield. The method involving the ether extraction (see above, p. 15) gave the 2'-nitro-2-iodobiphenyl in the best yields, which were on the order of 25-30 per cent.

A reaction, known as Niementowski's (18) reaction, yielded 2,2'-dinitrobiphenyl from the reaction of the diazonium salt of 2-nitroaniline with copper powder. It was thought that this reaction might occur with the diazonium salt of 2'-nitro-2-aminobiphenyl. This reaction was tried but only black sticky solid was obtained from which no identifiable product was obtained.

Since the yields of 2'-nitro-2-iodobiphenyl were not too good, 2'-nitro-2-bromobiphenyl was considered as a substitute compound. Mascarelli et al. (16) reported that this compound could be made better by an Ullmann reaction of 2-nitrobromobenzene and 2-iodobromobenzene than by the reaction of cuprous bromide on the diazonium salt of 2-nitro-2-aminobiphenyl; however, neither yield was listed.

The Ullmann coupling mentioned by Mascarelli was tried. 2-Nitrobromobenzene was reduced with hydrogen and platinum oxide to 2-bromoaniline in 51 per cent yield. The 2-bromoaniline, upon diazotization and a subsequent Sandmeyer reaction, afforded 2-iodobromobenzene in

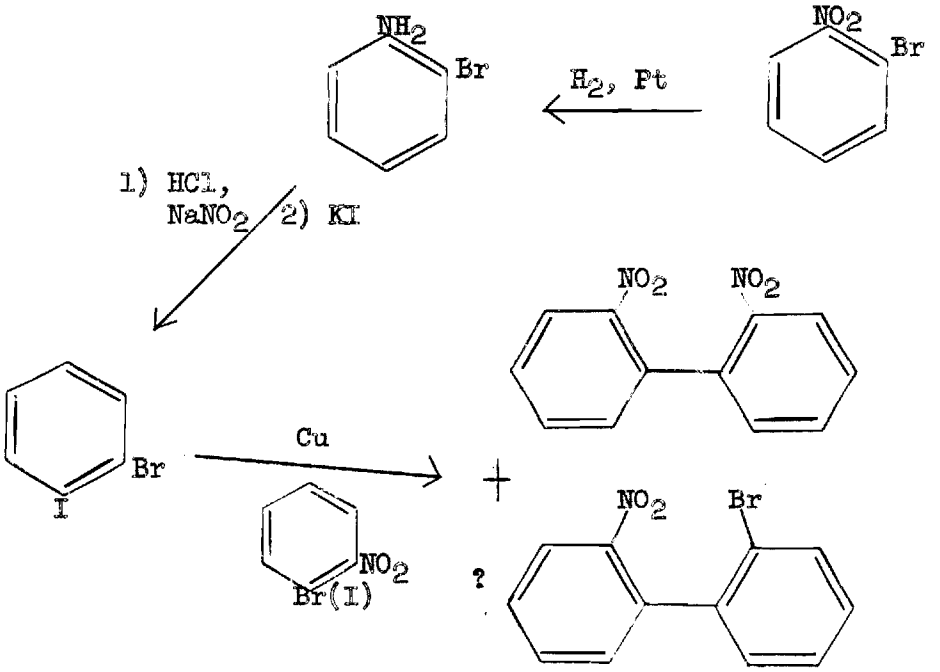

Figure 12. The Attempted Preparation of 2'-Nitro-2-bromobiphenyl

70 per cent yield. The Ullmann reaction of 2-nitrobromobenzene and 2-iodobromobenzene in dimethylformamide solution gave only

2,2'-dinitrobiphenyl. When this reaction was tried using a one to one mole ratio of 2-nitrobromobenzene to 2-iodobromobenzene with 44F copper powder at 240-260°C., a small amount of yellow oily crystals melting between 50-55°C. was obtained. Mascarelli et al. (16) listed the melting point of 2'-nitro-2-bromobiphenyl as 66-67°C. A similar reaction, but with a two to one mole ratio of 2-nitrobromobenzene and 2-iodobromobenzene gave a small amount of yellow oily crystals melting from 55-65°C. The reaction of a two to one mole ratio of 2-nitroiodobenzene and 2-iodobromobenzene with copper powder gave nothing melting near the melting point of 2'-nitro-2-bromobiphenyl, but some material melting from 110-115°C.

The action of cuprous bromide upon the diazonium salt of 2'-nitro-2-aminobiphenyl gave a black solid. Extraction of this black solid with cyclohexane yielded neither 2'-nitro-2-bromobiphenyl nor any definite product. Angeletti (1) reported a similar result in the attempted preparation of 6'-nitro-6-bromo-2,2'-bitolyl.

Since the attempted preparations of 2'-nitro-2-bromobiphenyl gave unsatisfactory results, the approach to tetraphenylene by means of 2'-nitro-2-iodobiphenyl was resumed, and the Ullmann coupling of this compound was investigated.

2'-Nitro-2-iodobiphenyl in dimethylformamide solution was heated at reflux (which was about 155°C.) with 44F copper powder. After the reaction 80 per cent of the starting material was recovered. When this reaction in dimethylformamide solution was run in a sealed tube at a temperature near 220°C., only oily material was obtained. Nothing from the oil was identified. In nitrobenzene solution, which refluxed near

204°C., the Ullmann reaction of 2'-nitro-2-iodobiphenyl yielded 50 per cent of the starting material, and no other material was identified.

When 2'-nitro-2-iodobiphenyl was heated with 44F copper in the range of 220-230°C., a compound labeled SDL V was obtained. SDL V was a light yellow crystalline material when recrystallized from ethanol. The highest melting point observed for a sample of these crystals was 188.5-189.5°C. SDL V contained nitrogen and no halogen, and was analyzed

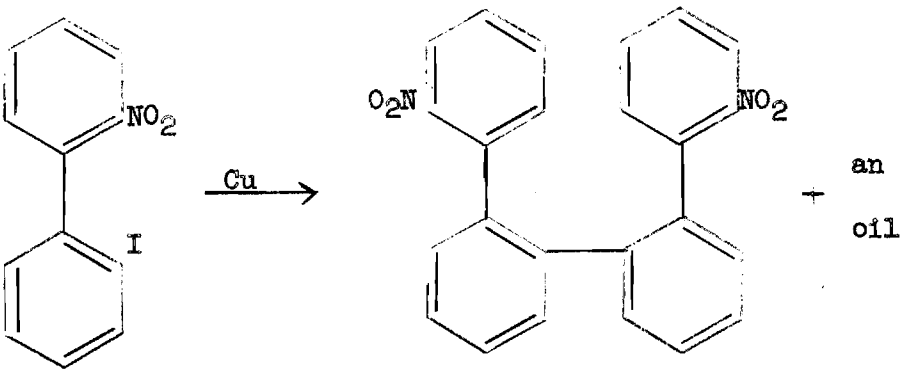

Figure 13. The Preparation of
2,2'-Di(2-nitrophenyl)biphenyl

for its composition. The agreement in per cent composition between the experimental and calculated values was reasonable, and hence SDL V was taken to be 2,2'-di(2-nitrophenyl)biphenyl. The per cent yields in the preparation of 2,2'-di(2-nitrophenyl)biphenyl were generally near 15 per cent, but when a fresh supply of 44F copper powder was used, the yield increased with the highest being 30 per cent.

Since the overall yield of 2,2'-di(2-nitrophenyl)biphenyl from the starting material, 2-nitrochlorobenzene, is only about 1.2 per cent,

another approach to this tetraphenyl system might give a better yield. Compounds for this approach would likely be formed by an unsymmetrical Ullmann reaction. A review of Fanta's (6) compilation of Ullmann reactions indicated no compound except 2'-iodo-2-carboxybiphenyl for this approach. This compound was reported by Shuttleworth and Rapson (23) to be formed in 30 per cent by the reaction of ortho-diiodobenzene and methyl 2-iodobenzoate with copper powder. Diphenic acid and 2,2'-diiodobiphenyl were also listed as products.

This reaction was tried. The 2-nitroiodobenzene was reduced with stannous chloride to 2-iodoaniline in 62 per cent yield. Catalytic reduction gave a lesser yield. The 2-iodoaniline upon diazotization and subsequent Sandmeyer reaction gave ortho-diiodobenzene in 51 per cent yield. ortho-Phenylenediamine upon diazotization and subsequent Sandmeyer reaction yielded no discernible ortho-diiodobenzene. Methyl 2-iodobenzoate and ortho-diiodobenzene in a one to two mole ratio were heated with copper powder in the 290-305°C. range. The higher boiling products were hydrolyzed with potassium hydroxide. Yellow crystals melting at 147.5-149.5°C. and some white crystals melting above 215°C., probably impure diphenic acid, were obtained. Shuttleworth and Rapson (23) report 149-150°C. as the melting point of 2'-iodo-2-carboxybiphenyl. Although the quantities of reactants were varied somewhat in this reaction, the yield of 2'-iodo-2-carboxybiphenyl was never more than 7.3 per cent. Yields of this size did not give a better approach to the tetraphenyl system.

The approach to tetraphenylene was resumed by trying the reduction of 2,2'-di(2-nitrophenyl)biphenyl to 2,2'-di(2-aminophenyl)biphenyl.

This reaction was attempted with hydrogen and platinum oxide. In benzene solution the complete reduction of this compound, as evidenced

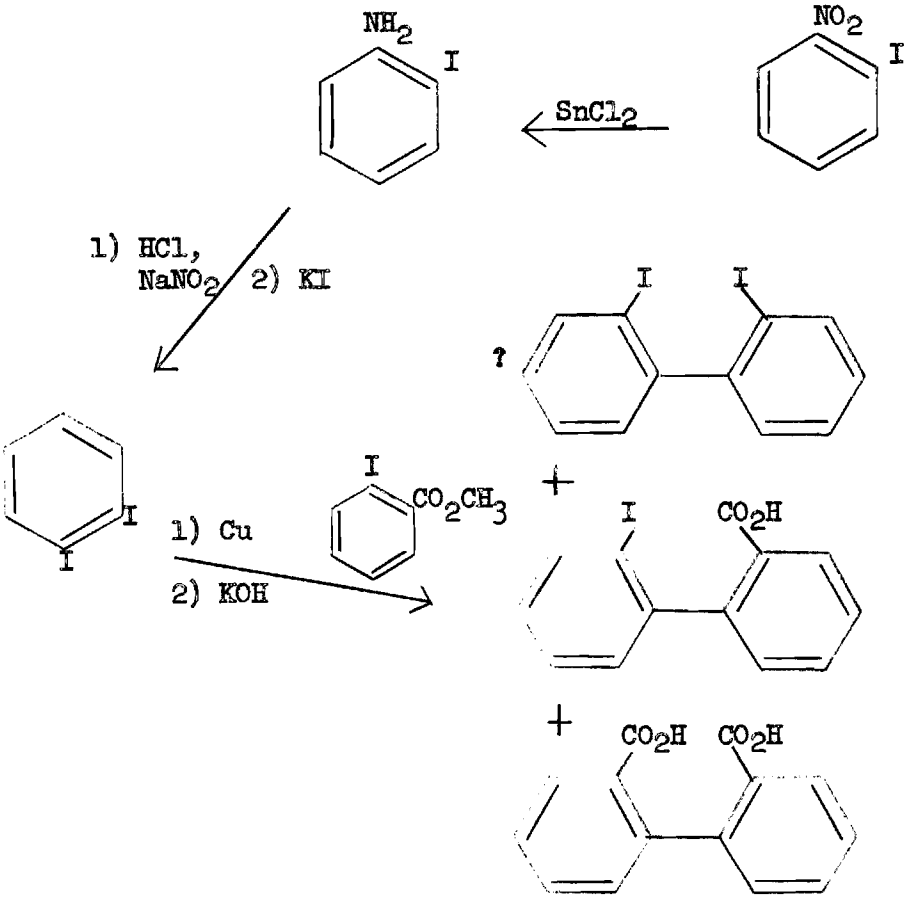

Figure 14. The Preparation of 2'-Iodo-2-carboxybiphenyl

by the uptake of hydrogen, was difficult to effect. The reaction product, a red oil, failed to crystallize from solvents; however, a white solid melting around 66-70°C. was precipitated from a hydrochloric acid solution of the red oil using ammonium hydroxide. This solid, SDL VI, gave a positive beta-naphthol test. The reduction was also carried out to completion in dioxane solution. Again most of the time a red oil was

obtained. As before, SDL VI could be precipitated from acid solutions of the oil. This white solid was found later to contain considerable ammonium chloride. Once, the dioxane solution, after dilution with

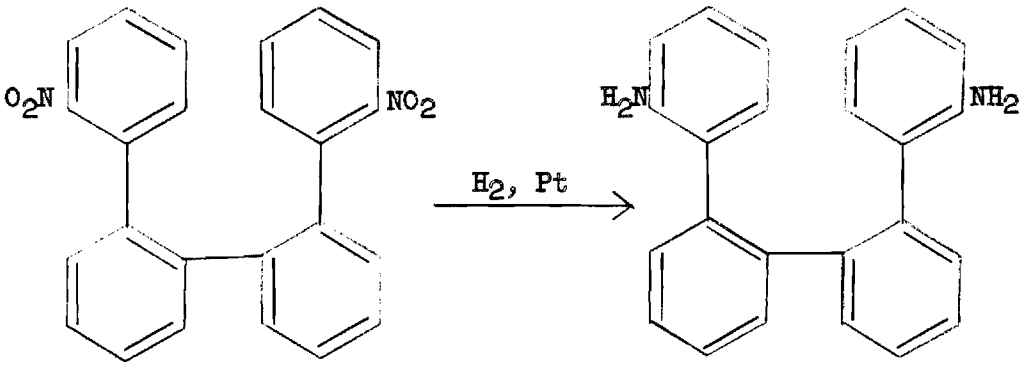

Figure 15. The Preparation of 2,2'-Di(2-aminophenyl)biphenyl

water and evaporation, yielded pink-white crystals. A sample of these crystals were vacuum sublimed to give a white solid melting at 138.0-139.5°C. This solid was analyzed for nitrogen and was found to contain 8.24 and 8.17 per cent, which was close to the calculated value of 8.33 per cent nitrogen in 2,2'-di(2-aminophenyl)biphenyl.

In the latter part of the project the catalytic reduction of 2,2'-di(2-nitrophenyl)biphenyl was carried out in ethanol. Although the reactant was not very soluble in ethanol, complete reduction in this solvent was achieved in a relatively short time. From this reaction white crystals melting at 140-141°C. were obtained in 22.8 per cent yield, and a second crop of white crystals melting between 130-135°C. were also obtained. The material melting near 140°C. was taken to be 2,2'-di(2-aminophenyl)biphenyl.

Various samples of SDL VI which were thought to contain 2,2'-di(2-aminophenyl)biphenyl were used in attempts to prepare 2,2'-di-(iodophenyl)biphenyl. The sample of SDL VI melting near 66-70°C. upon diazotization and treatment with potassium solution gave a yellow material which melted indistinctly around 60-80°C. This material labeled SDL VII gave a positive test for halogen and a negative test for nitrogen, and attempts to recrystallize it were unsuccessful.

2,2'-Di(2-aminophenyl)biphenyl melting at 138.0-139.5°C. upon diazotization and treatment with potassium iodide solution yielded a yellow solid which, after vacuum sublimation melted at 109-110°C. This material contained 25.3 and 24.8 per cent iodine, which is much lower than the 45.5 per cent calculated for 2,2'-di(2-iodophenyl)-biphenyl. The diazotization and Sandmeyer reaction was repeated with a sample of the amine melting at 138-140°C. This reaction yielded a product which after vacuum sublimation melted around 65-70°C. This material recrystallized from ethanol to give white crystals melting at 145.0-146.5°C. The attempts at recrystallization before the vacuum sublimation were unsuccessful. These crystals were analyzed. The composition did not agree with the composition of 2,2'-di(2-iodophenyl)-biphenyl, but it did agree reasonably well with the composition of 2'-phenyl-2-(2-iodophenyl)biphenyl. The crystals were taken to be 2'-phenyl-2-(2-iodophenyl)biphenyl because of this agreement. Perhaps 2,2'-di(2-iodophenyl)biphenyl was formed and one iodo group was reduced from the ring with excess hydriodic acid. Shoesmith and Slater (22) reported that ortho-iodotoluene was deiodinated in 48.4 per cent yield by hydriodic acid in one day of reaction at 25°C. They also report

that ortho-toluene is deiodinated more rapidly than the para isomer and much more rapidly than the meta isomer. The yields in the preparation

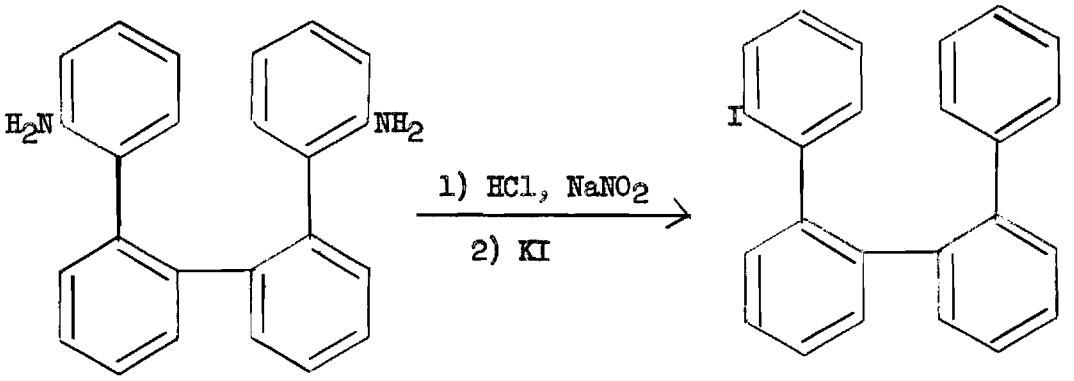

Figure 16. The Preparation of 2'-Phenyl--2-(2-iodophenyl)biphenyl

of 2'-phenyl-2-(2-iodophenyl)biphenyl were quite small being less than 10 per cent.

When SDL VII was heated with copper powder, a very small amount of a white solid melting at 203-207°C. was sometimes obtained, and was

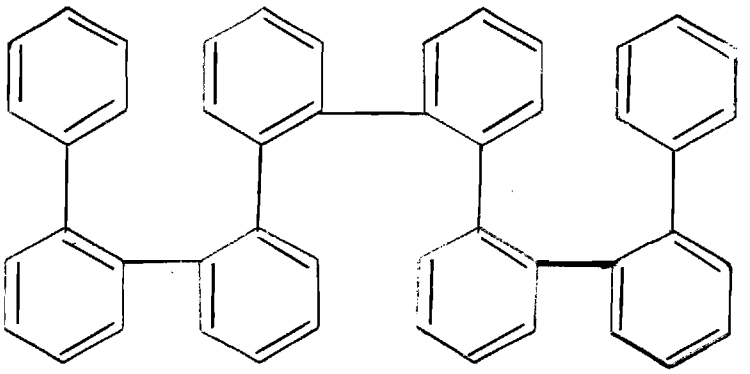

Figure 17. ortho-Octaphenyl

labeled SDL VIII. This solid gave a negative Beilstein's test for

halogen. This product may be ortho-octaphenyl, which would result from a usual Ullmann reaction of 2'-phenyl-2-(2-iodophenyl)biphenyl.

CHAPTER III

EXPERIMENTAL

Copper Powder

In the earlier part of this project the copper powder used was Baker's precipitated powder.[1] It is designated as Baker's copper in this thesis. The most frequently used copper powder was prepared by Malone Metal Powder Company, Flemington, New Jersey, and labeled 44F, the designation used in this thesis. This powder gave good yields in the Ullmann reaction (12); however, after it aged, yields in the Ullmann reaction decreased.

A sample of copper powder was prepared by dissolving 800 g. of copper sulfate pentahydrate in four liters of water and by sprinkling slowly into this solution 210 g. of powdered zinc. This copper powder gave no yield of 2,2'-dinitrobiphenyl when reacted with 2-nitrochlorobenzene in dimethylformamide solution.

A sample of commercial copper powder of unknown origin gave yields of 60-70 per cent in the reaction of 2-nitrochlorobenzene to 2,2'-dinitrobiphenyl in dimethylformamide solution.

Copper designated as treated was subjected to the process of Kleider and Adams (11). Copper powder weighing 200 g. was washed with 500 ml. of a two per cent solution of iodine in acetone and then

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[1] J. T. Baker Chemical Co., Phillipsburg, New Jersey.

filtered. The copper was then washed with 500 ml. of a 1:1 concentrated hydrochloric acid-acetone solution followed by washing with four to five approximately 50 ml. portions of acetone. After filtering it was dried in a vacuum desiccator. The copper was used immediately or after a four-hour interval for a second addition. Since the 1:1 concentrated hydrochloric acid-acetone suspension of 44F copper powder was not readily filtered, pure acetone was substituted for the acidic acetone solution. This gave a copper which is designated as partially treated copper powder.

The Preparation of 2,2'-Dinitrobiphenyl

Without dimethylformamide.--The procedure for this preparation came mainly from Organic Syntheses (7). To 100 g. of 2-nitrochlorobenzene heated in a 500 ml. flask to 215-225°C. with an electric heating mantle, was added 100 g. of treated Baker's copper powder. The addition took one hour during which time the reaction was mechanically stirred. After letting the reaction continue for three hours it was permitted to cool and was washed first with 700 ml. and then with 500 ml. of hot 95 per cent ethanol. Upon concentration and cooling of this ethanol, dark crystals were obtained. These were treated with decolorizing carbon and were recrystallized from 95 per cent ethanol and yielded 25.5 g. of light yellow crystals, m. p. 124-125°C.[2] This is a 33 per cent yield.

Using dimethylformamide and 44F copper powder.--This procedure was taken from that of Kornblum (12). 2-Nitrochlorobenzene, weighing 100 g., and

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[2]All melting points are uncorrected.

500 ml. of dimethylformamide were added to a one-liter three-necked, round-bottomed flask equipped with a heating mantle, condenser, and a mechanical stirrer. Partially treated 44F copper powder, weighing 100 g., was added and the mixture was heated at reflux, approximately 150-155°C., for four hours. At this time 100 g. more of copper powder was added and the reaction was refluxed for four additional hours. The reaction was allowed to cool to below 100°C. and the reaction mixture was filtered from the copper sludge. The filtrate was poured into eight liters of water and was allowed to stand overnight. During this period solid had separated from the water. This solid was filtered from the water and was dissolved for the most part in 500 ml. of hot acetone. The acetone solution was filtered from the copper salts and, after evaporation and cooling, yielded dark and sometimes rhombic crystals. These crystals were dissolved in one liter of boiling 95 per cent ethanol and were treated with decolorizing carbon. Evaporation and cooling of the ethanol gave light yellow crystals, m. p. 124-125°C. The best yields of this reaction were approximately 75 per cent; Kornblum (12) reports 80 per cent. The yields of this reaction decreased over a long period to 35 per cent after the 44F copper powder was at least three years old. A more recent order of 44F copper powder in October, 1958, gave yields of 47-56 per cent. A quantity of commercial copper of unknown origin gave yields of 70-75 per cent.

2-Bromonitrobenzene once was used to prepare 2,2'-dinitrobiphenyl by the above procedure except that Baker's copper powder was used. The yield from this reaction was 40 per cent.

The Preparation of 2,2'-Diaminobiphenyl

By the chemical reduction of 2,2'-dinitrobiphenyl.--2,2'-Dinitrobiphenyl weighing 25.5 g., 35 g. of powdered iron, and 100 ml. of 50 per cent aqueous ethanol were added to a one liter three-necked flask equipped with a mechanical stirrer and an electric heating mantle. While it was stirred, the mixture was heated to boiling, and during a period of 45 minutes a solution of 50 ml. of concentrated hydrochloric acid and 50 ml. of 50 per cent ethanol was added. The reaction mixture was heated at reflux for three hours, after which it was filtered while hot. The filtrate was made basic with sodium hydroxide, and a precipitate formed. The precipitate was washed with approximately 50 ml. benzene; the benzene which slowly separated was collected and was evaporated to give crystals, m. p. 70-75°C. The iron sludge was washed twice with 95 per cent ethanol which upon evaporation gave more crystals, m. p. 70-75°C. The combined crystals weighed 10.6 g. They were somewhat dark and were recrystallized from 95 per cent ethanol to give 7.0 g. of gray-brown crystals, m. p. 78-80°C. for a 36.3 per cent yield.

By the catalytic reduction of 2,2'-dinitrobiphenyl.--Into 300 ml. of thiophene-free benzene[3] was dissolved 21 g. of 2,2'-dinitrobiphenyl. The benzene solution of the nitro compound was divided into two equal parts and 0.5 g. of platinum oxide was added to each. These solutions were hydrogenated on a Parr pressure apparatus until no more hydrogen was consumed. After combination and evaporation of the benzene solutions,

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[3]One l. of benzene was extracted first with two 250 ml. portions of concentrated sulfuric acid and second with two 250 ml. portions of water. The benzene was then distilled.

8.0 g. of white crystals, m. p. 78-80°C., came from the solution. Further concentration of the benzene yielded more crystals, which were recrystallized from ethanol. These latter crystals, m. p. 78-80°C., were white and weighed 4.5 g. The 12.5 g. of white crystals was a 79 per cent yield. Other yields for the same reaction varied from 71 per cent to 89 per cent.

The Preparation of 2,2'-Biphenyleneiodonium Iodide and 2,2'-Diiodobiphenyl and Their Reactions with Copper

Which yielded biphenylene.--2,2'-Diaminobiphenyl weighing 7.0 g. and 44 ml. of concentrated hydrochloric acid were added together in a 500 ml. three-necked flask and were heated to 60-70°C. for one hour. The flask was then equipped with a mechanical stirrer and a dropping funnel and was surrounded by an ice-salt bath. After the mixture had cooled to -7°C., a solution of 17 g. of sodium nitrite in 40 ml. of water was added slowly through the funnel while the solution was being stirred. The addition lasted for two hours and the reaction temperature was kept below -4°C. After this reaction period, the mixture was poured into a cold solution of 25 g. of potassium iodide in 25 ml. of water whereupon a foamy black mass was formed. The mixture was heated to 75-80°C. and iodine vapors were expelled. The mixture was washed with a sodium thiosulfate solution and was left in contact with this solution overnight. The black mass was filtered from the solution and, after drying, it weighed 13.8 g. A small sample of the black solid was dissolved in water and upon cooling the solution yielded a yellow solid, m. p. 203-206°C. (15). The bulk of the black solid was washed with a total of

500 ml. of acetone. While the solid did not dissolve very extensively, the wash acetone was quite dark. This washing left a gray solid weighing 8.0 g. for a 51.7 per cent yield assuming the product to be pure 2,2'-biphenyleneiodonium iodide.

In a 50 ml. round-bottomed flask with a 1.5 cm. diameter side arm just above the body of the flask was placed 4.0 g. of 2,2'-biphenyleneiodonium iodide thoroughly mixed with 11.4 g. of treated Baker's powder. By means of an electric heating mantle the mixture was heated for one hour at around 200°C. although the temperature once rose to 300°C. Near 180°C. vapors appeared from the reaction and condensed in long yellow-white needles in the top of the flask and in the side arm. The needles, m. p. 109-111°C., were taken to be biphenylene (15). A small sample of these crystals was dissolved in absolute ethanol and a few drops of saturated ethanolic picric acid was added. Upon evaporation of the ethanol red crystals formed and were recrystallized from ethanol to give the pure product of m. p. 111-112°C. (15).

Which gave biphenylene sulfide.--2,2'-diaminobiphenyl weighing 37 g. and 127 ml. of concentrated hydrochloric acid were added to a one liter three-necked flask and were heated gently for one hour. The flask was now equipped with a mechanical stirrer, a dropping funnel, and an ice-salt bath. After the mixture had cooled to -9°C., a solution of 32 g. of sodium nitrite in 117 ml. of water was added through the funnel while the reaction was being stirred. The sodium nitrite solution was added over a period of three hours and the reaction temperature was kept below -3°C. After allowing the solution to react twenty minutes more, it was poured into a solution of 80 g. of potassium iodide in

80 ml. of water. A bubbling black mass appeared. This product and solution were heated to 80°C. to expel vapors. The black mass was washed with a sodium thiosulfate solution and was left in the solution overnight. After filtering the sodium thiosulfate solution from the black solid, the solid was washed with 50-100 ml. portions of acetone totaling 500 ml. until the solid was somewhat lighter in color. In the process of recovering the acetone, the cooling of the concentrate yielded crystals, and the further cooling yielded more. These crystals were recrystallized twice from 95 per cent ethanol to give white needles, m. p. 109°C. These crystals were taken to be 2,2'-diiodobiphenyl (15). The gray solid, 2,2'-biphenyleneiodonium iodide, was washed further with acetone but upon evaporation and cooling no more 2,2'-diiodobiphenyl was obtained. The final weight of the 2,2'-biphenyleneiodonium iodide was 30.4 g.; this was a yield of 45 per cent considering both products.

To a 500 ml. three-necked flask were added 15 g. of 2,2'-biphenyleneiodonium iodide, prepared in the last paragraph, and 66 ml. of dimethylformamide; the solution was heated to reflux and 13 g. of treated 44F copper powder was added. After four hours of heating at reflux 155°C., 13 g. more of copper powder was added and the reaction was heated for eight more hours. The reaction mixture was cooled to less than 50°C. and poured into two liters of water. The residue which separated from the water was extracted with hot 95 per cent ethanol, and upon evaporation and cooling, the ethanol yielded 4.0 g. of yellow needles, m. p. about 80°C. After treatment with decolorizing carbon and recrystallization from 95 per cent ethanol four times, pale yellow

crystals, m. p. 98.0-98.5°C., were obtained. A sample of these crystals was sublimed at room pressure to give crystals, which after being recrystallized from ethanol twice, gave white needles, m. p. 98.0-98.5°C. This compound was designated as SDL I. A sodium fusion showed that SDL I contained sulfur and no halogen nor nitrogen. Analysis calculated for $C_{12}H_8S$: carbon, 77.8; hydrogen, 4.36; and sulfur, 17.4; and molecular weight 184. Found: carbon, 78.2; hydrogen, 4.42; and sulfur (by difference) 17.8 and molecular weight 181. A small sample of SDL I was brominated by adding it to a solution of bromine in acetic acid. After the addition of water to the acetic acid solution a solid precipitated. It was recrystallized from 95 per cent ethanol twice to give a solid, m. p. 223°C. (4). SDL I was considered to be biphenylene sulfide.

Which yielded 2,2'-diiodobiphenyl.--The reaction of the last paragraph was repeated using 21.5 g. of 2,2'-biphenyleneiodonium iodide which had not been washed with sodium thiosulfate. The reaction product was placed in two l. of water and allowed to stand overnight. The residue left was removed and was extracted with hot acetone. After concentration and cooling of the acetone, it yielded a white solid, m. p. 60-65°C., which contained iodine and no sulfur. After six recrystallizations from 95 per cent ethanol the material, m. p. 104-105°C., was white and crystalline; this material was assumed to be impure 2,2'-diiodobiphenyl.

A 500 ml. flask was equipped with an electric heating mantle, a mechanical stirrer, and a condenser. Eight g. of 2,2'-diiodobiphenyl and 50 ml. of dimethylformamide were added to the flask. After the

solution was heated to 125°C., 8.0 g. of treated 44F copper powder was added over a period of a few minutes and the mixture was heated for an additional four hours. The hot mixture was filtered and the residue was washed with dimethylformamide. The filtrate and wash was poured into one liter of water and was permitted to stand overnight. The residue which had appeared in the water was extracted with hot 95 per cent ethanol, which upon evaporation gave crystals, m. p. 100-103°C. The crystals were treated with decolorizing carbon and recrystallized from ethanol to give gray-white crystals, m. p. 109°C. A sodium fusion gave a negative test for sulfur and a yellow precipitate with silver nitrate. It was concluded that this was the starting material, 2,2'-diiodibiphenyl, because of a very similar melting point and because it contained iodine.

The Preparation and Attempted Preparations of 2'-Nitro-2-aminobiphenyl from 2,2'-Dinitrobiphenyl

To give diphenazonmonoxide.--This procedure was taken from that of Purdie (19). To a three-liter round-bottomed flask equipped with a condenser and a heating mantle was added 1.1 l. of 95 per cent ethanol and 84 g. of 2,2'-dinitrobiphenyl. This mixture heated until a solution was formed. After 295 g. of sodium sulfide nonahydrate was dissolved in 300 ml. of water 24 g. of sulfur was added to the sulfide solution and the whole heated until all of the sulfur had dissolved. This sodium polysulfide solution was added slowly through the condenser to the dinitrobiphenyl and the mixture was refluxed for three hours and then permitted to stand overnight. About 600 ml. of ethanol and water was boiled from

the solution and the remainder of the solution was poured into two liters of ice water and allowed to stand overnight. The residue which appeared was filtered from the water and was washed with ether. The ether solution, which was red-orange, was washed with water and dried over sodium hydroxide flakes. Upon evaporation of the ether, a small amount of residue remained. This residue was dissolved in 95 per cent ethanol and, after evaporation of the ethanol, a red-orange solid was obtained, m. p. 77-83°C.

The ether insoluble residue was dissolved in hot or boiling 95 per cent ethanol and treated with decolorizing carbon. Upon cooling, the ethanol solution yielded yellow needles, m. p. 135-136°C. These were recrystallized twice from 95 per cent ethanol and yielded crystals having a m. p. of 137.0-137.5°C. A sample of these was fused with sodium, and gave a positive test for nitrogen and a negative test for halogen and sulfur. Analysis calculated for $C_{12}H_8N_2O$: carbon, 73.4; hydrogen, 4.08; and nitrogen, 14.3. Found: carbon, 73.24; hydrogen, 4.08; and nitrogen, 14.41.

This formula fits diphenazonmonoxide, m. p. 139°C., which was prepared by Ullmann and Dieterle (25) by the reduction of 2,2'-dinitrophenyl with sodium sulfide in ethanol solution.

To give a unrecrystallizable red oil.--From the results of the previous procedure it was assumed that when Purdie (19) specified 48 g. of sodium sulfide, he used the nonahydrate. To a one-liter round-bottomed flask equipped with a condenser and a heating mantle were added 42 g. of 2,2'-dinitrobiphenyl and 600 ml. of 95 per cent ethanol. This solution was heated to reflux and a solution prepared by heating 48 g. of sodium

sulfide nonahydrate and 12 g. of sulfur in 150 ml. of water was added slowly to the ethanol solution. After three hours of refluxing the solution was permitted to cool and to stand overnight. About 400 ml. of the solvents was distilled off and the remaining solution poured into one liter of ice water and allowed to stand overnight. A residue formed and was filtered from the solution. When washed with ether, most of this residue dissolved. The ether solution was washed with three portions of water and was dried over solid sodium hydroxide. Upon evaporation of the ether there remained a red oil but no crystals. The red oil could not be crystallized from ethanol, acetone, benzene, water-ethanol mixtures, or cyclohexane; in each case the red oil was obtained again. When concentrated hydrochloric acid was added to the oil, a light yellow solid was formed. When this solid had been washed with ether and dried, it had a decomposition point of 210-215°C. The solid, which was probably an amine hydrochloride, did undergo a diazotization reaction. The solid was somewhat soluble in water, and when sodium hydroxide was added to its water solution a small amount of solid formed. This latter solid was dissolved in 95 per cent ethanol and upon complete evaporation of the alcohol yielded yellow crystals, m. p. 65-67°C. These crystals may well have been 2'-nitro-2-aminobiphenyl, but at the time the author was looking for red-orange crystals, m. p. 95-96°C. as described by Purdie (19).

Which produced 2'-nitro-2-aminobiphenyl.--The initial steps in this procedure are the same as the preceding preparation. Concentrated hydrochloric acid was added to the ether solution which previously had been washed with water and dried over sodium pellets. The light

yellow hydrochloride was formed in the ether. After filtering the hydrochloride from the ether solution and letting it dry, it and about 20 ml. of concentrated hydrochloric acid were added to 500 ml. of water. Upon heating the mixture the hydrochloride went into solution, but left a red tar which was removed by filtration. After the solution was cooled to approximately 5°C., dilute ammonium hydroxide was added to the solution until a suspension formed. When the suspension appeared in the solution, the solution was again cooled and a fluffy yellow solid usually formed. If the solid did not form, more ammonium hydroxide was added and the solution cooled until the solid did appear. More ammonium hydroxide was added until the solidification was complete. If the neutralization of the amine hydrochloride was carried out hurriedly, a red oil was the product. The solid was filtered off and allowed to dry. The yellow solid, m. p. 63-65°C., could be recrystallized from an ethanol-water mixture, but this was difficult to reproduce. This preparation was repeated many times and most of the yields ranged between 40 to 50 per cent. This yellow solid was taken to be 2'-nitro-2-aminobiphenyl in agreement with the m. p. of 64-65°C. reported by Fairfull et al. (5) which contradicted the report of Purdie (19).

The Alternate Synthesis of 2'-Nitro-2-aminobiphenyl

The preparation of 2-bromobenzoic acid.--This preparation was taken from Organic Syntheses (3). In a three-liter three-necked flask equipped with a condenser and a heating mantle were placed 1.7 l. of water, 150 g. of potassium permanganate, and 69 g. of 2-bromotoluene. The solution was heated slowly to boiling and was refluxed for five hours. At

this time the condenser was lowered and excess 2-bromotoluene amounting to 15 g. was distilled from the solution. The manganese dioxide sludge was filtered from the solution and was washed with two 125 ml. portions of hot water. After the solution had been concentrated to 450 ml., 65 ml. of concentrated hydrochloric acid was added to the solution making it acid to congo red paper. A white precipitate formed in the solution. After standing overnight the solid was filtered from the solution and dried, it was recrystallized from 300 ml. of toluene and hielded 37 g. of a white crystalline solid, m. p. 147.5-149.5°C. The yield was 58 per cent considering the recovery of some 2-bromotoluene.

The preparation of methyl 2-bromobenzoate.--Into 900 ml. of methanol, which in order to remove water had been refluxed over magnesium ribbon and then distilled (26), 153 g. of 2-bromobenzoic acid was dissolved. This solution was saturated with hydrogen chloride and then was refluxed for twelve hours. Most of the methanol was distilled off and, after cooling, the crude ester was washed with water and with ammonium hydroxide. The water and the ammonium hydroxide washings were acidified with concentrated hydrochloric acid and yielded 2-bromobenzoic acid, which, after recrystallization from water, weighed 17 g. After being dried over calcium chloride, the crude ester was distilled under reduced pressure; the fraction collected between 3-15 mm. of mercury pressure and between 138-148°C. was taken to be methyl 2-bromobenzoate. This weighed 127 g. and was a per cent yield of 87 considering the recovery of 2-bromobenzoic acid.

The preparation of 2-nitroiodobenzene.--Into a three-liter three-necked flask were placed 500 ml. of concentrated hydrochloric acid, 200 ml. of water, approximately 700 g. of ice, and 150 g. of 2-nitroaniline. The flask was surrounded with an ice bath and was equipped with a mechanical stirrer. After the mixture had cooled below -10°C. a solution of 78 g. of sodium nitrite in 400 ml. of water was added with stirring over a period of 45 minutes. The solution was allowed to react for two hours during which time 500 g. more of ice was added to keep the temperature of the solution below 5°C. Because of undissolved solid the solution was filtered, and a solution of 180 g. of potassium iodide in 200 ml. of water was added slowly to the clear solution. The reaction was vigorous, and a foaming brown mass formed atop the solution. After continued stirring all the solid settled to the bottom of the container. This solid was filtered from the solution and was allowed to dry. The brown solid was dissolved in 550 ml. of hot 95 per cent ethanol and was treated with carbon. Upon cooling, the solution yielded yellow crystals and a red-black solid. The red-black solid was redissolved in 95 per cent ethanol and treated with carbon; this solution on cooling also gave yellow crystals. The total amount of yellow crystals weighed 225 g. for an 80 per cent yield. The crystals had a m. p. of 47-49°C.

The preparation of 2'-nitro-2-carboxybiphenyl from 2-nitroiodobenzene and methyl 2-bromobenzoate.--Into a 500 ml. round-bottomed flask were placed 114 g. of methyl-2-bromobenzoate and 225 g. of 2-nitroiodobenzene, and the whole was heated to 240°C. During a period of two hours 160 g. of 44F copper powder was added slowly. In the first stages of the addition the temperature was kept from 250-260°C., but during the latter part of

the addition the temperature was kept in the 250-270°C. range since the reaction mixture was less volatile. After the addition of the copper the mixture was entirely sludge and was permitted to cool. When cooled to room temperature the copper sludge was washed with 1.5 l. of warm acetone. The acetone wash was concentrated to 300 ml. and then was distilled under reduced pressure. Between 225-235°C. and 5-10 mm. of mercury pressure a fraction, which was a yellow syrup and weighed 120 g., was obtained. This yellow syrup, 250 ml. of 95 per cent ethanol, and 35 g. of potassium hydroxide in 250 ml. of water were added together in a one-liter round-bottomed flask equipped with a heating mantle and a condenser and were heated at reflux for 16 hours. The solution was allowed to cool for five hours, during which time a solid had formed in the solution. The solid was filtered off and the filtrate was poured into 2.5 l. of water and was allowed to stand overnight. A solid had appeared and was filtered from the solution. To the solution was added 75 ml. of concentrated hydrochloric acid and a precipitate occurred. This precipitate was dissolved in 16 per cent aqueous ethanol and the solution was cooled. On successive evaporation and filtration, the solution yielded three crystalline fractions: the first had a m. p. of 157-160°C., the second of 143-148°C., and the third of 128-132°C.

The first portion was almost completely dissolved in a sodium hydroxide solution and was reprecipitated with hydrochloric acid; it weighed 37 g. and had a m. p. of 162-165°C. The second and third portions did not dissolve to any noticeable extent in sodium hydroxide solution and were discarded. Part of the crystals from the first portion, m. p. 162-165°C., was dissolved in hot toluene which, upon cooling,

yielded 20 g. of yellow-green crystals, m. p. 165-166°C. This was taken to be 2'-nitro-2-carboxybiphenyl (23). The 37 g. of product which had a m. p. 162-165°C. was a 26.7 per cent yield as based on the starting quantity of methyl 2-bromobenzoate.

The preparation of 2'-nitro-2-carboxamidobiphenyl from 2'-nitro-2-carboxylbiphenyl.--For a period of an hour 20 g. of 2'-nitro-2-carboxylbiphenyl and 80 ml. of thionyl chloride were refluxed in a 250 ml. flask. After the solution had cooled it was added to 300 ml. of concentrated ammonium hydroxide whereupon a solid appeared. This solid was washed with water and with sodium hydroxide. When the dry solid was dissolved in 100 ml. of toluene and cooled there was obtained 16 g. of yellow-green crystals, m. p. 136.5-137.5°C. This was a per cent yield of 80.

The preparation of 2'-nitro-2-aminobiphenyl from 2'-nitrocarboxamidobiphenyl.--2'-Nitro-2-carboxamidobiphenyl weighing 5.0 g. was ground to a powder and placed along with 8.0 g. of sodium hydroxide and 50 ml. of water in a 500 ml. flask. After the sodium hydroxide dissolved, 2.0 g. of bromine was added. With stirring the mixture was heated at 50-55°C. for one hour. Nine g. of additional solid sodium hydroxide was added, and the temperature was kept in the 70-80°C. range for another hour. When the mixture had stood overnight, a red oil containing some solid had settled to the bottom of the flask. After separating the oil and solid mixture from the reaction solution it was washed with toluene which dissolved the oil and left the solid. This solid had a m. p. of 128-132°C.; it was taken to be unreacted starting material. The red oil would not crystallize from toluene or ethanol; upon concentration of

these solvents the red oil would return. However, the oil did dissolve in the 6 N hydrochloric acid, and after this acid solution was made basic with ammonium hydroxide, it yielded yellow needles on standing. These needles, m. p. 62-65°C., upon treatment with acetylchloride and crystallization of the product from ethanol gave an acetamide, m. p. 157-158°C., which is in agreement with the acetamide of 2'-nitro-2-aminobiphenyl, m. p. 159-160°C. reported by Purdie (19). With a m. p. of 64-65°C. for 2'-nitro-2-aminobiphenyl reported by Fairfull et al. (5) and the similarity of the m. p. of the acetyl derivatives, the product of this reaction was taken to be 2'-nitro-2-aminobiphenyl.

The Preparations and Attempted Preparations of 2'-Nitro-2-iodobiphenyl In hydrochloric acid solutions.--A sample of the amine hydrochloride of impure 2'-nitro-2-aminobiphenyl weighing 24 g., 40 ml. of concentrated hydrochloric acid, and 150 ml. of water were added to a 500 ml. three-necked flask equipped with a heating mantle and a mechanical stirrer. The mixture was warmed and all material went into solution. The heating mantle was replaced with an ice-salt bath. As the solution cooled to -8°C., the hydrochloride precipitated. A solution of 9.0 g. of sodium nitrite in 30 ml. of water was added with stirring over a period of one hour. After permitting the mixture to react for an additional hour, it was poured into a solution of 18 g. of potassium iodide in 18 ml. of water. The reaction was somewhat violent; a bubbling black mass appeared atop the solution. After the reaction the reaction mixture was heated and gases were evolved. The black solid was filtered and dried and an attempt was made to recrystallize the

black solid from cyclohexane. Evaporation of the cyclohexane left a residue which was washed with carbon tetrachloride. Upon evaporation, the carbon tetrachloride left a brown solid which was recrystallized from cyclohexane and yielded 1.6 g. of yellow-brown crystals, m. p. 75-76°C. These crystals were recrystallized from 95 per cent ethanol to give tan crystals, m. p. 76-77°C.

This procedure involved a frequently used cyclohexane extraction. 2'-Nitro-2-aminobiphenyl weighing 14 g., 30 ml. of concentrated hydrochloric acid, and 100 g. of ice were added together in a 500 ml. three-necked flask equipped with a mechanical stirrer and surrounded by an ice bath. To this mixture a solution of 5.0 g. of sodium nitrite in 20 ml. of water was added slowly with stirring. The reaction was let to proceed for one hour and then a solution of 20 g. of potassium iodide was added to it. A black foamy solid appeared and, after the reaction had subsided, was filtered from the solution. After drying, the black solid was placed in a Soxhlet and was extracted for 24 hours with cyclohexane. Apparently not much of the black solid dissolved. The black solid was fused with sodium and tests which were positive for nitrogen and negative for halogen were obtained. The cyclohexane was evaporated completely and dark crystals remained. These were dissolved in 95 per cent ethanol and treated with carbon. When the ethanol solution was concentrated, it yielded light yellow crystals weighing 2.0 g. and having a m. p. of 81-82°C. This reaction was run many times with some variations in procedure. Most yields were near ten per cent and no yield was significantly better.

Twenty-one g. of 2'-nitro-2-aminobiphenyl, 30 ml. of water, and 25 g. of ice were placed in a one-liter three-necked flask equipped with a mechanical stirrer and surrounded by an ice bath. After the mixture had cooled below -5°C., a solution of 5.6 g. of sodium nitrite in 20 ml. of water was added slowly with stirring. After the solution had reacted for two hours, it was filtered to remove unreacted starting material. Part of this diazonium solution was made neutral to litmus with ammonium hydroxide; a brown precipitate formed as the solution approached neutrality. As a solution of 7.0 g. of potassium iodide in 20 ml. of water was added to the solution containing the brown precipitate, a reddish purple precipitate formed while the brown one disappeared. The maroon solid was filtered from the solution and was permitted to dry for a few minutes. It was placed in a Soxhlet extractor to be extracted with cyclohexane. Before the cyclohexane had come in contact with the maroon solid, the solid exploded. It was assumed that the material was by no means 2'-nitro-2-iodobiphenyl, but that it might have been 2'-nitro-2-diazoniumbiphenyl iodide. All remaining samples of this exploding material were dissolved in acetone which, as evidenced by the evolution of gases, decomposed it. Evaporation of the acetone yielded a black tar, from which nothing was obtained.

This procedure gave the best yields of 2'-nitro-2-iodobiphenyl. To a one-liter three-necked flask equipped with a mechanical stirrer and surrounded by an ice bath were added 12 g. of 2'-nitro-2-aminobiphenyl, 135 ml. of concentrated hydrochloric acid, and 450 g. of ice. After the solution had cooled below -15°C., a solution of 4.5 g. of

sodium nitrite in 20 ml. of water was added slowly with stirring over a period of ten minutes. At the end of one hour not quite all of the solid had dissolved, so the solution was filtered and added slowly by means of a dropping funnel to a solution of 40 g. of potassium iodide, 75 ml. of water, and 7.0 ml. of concentrated sulfuric acid. Various colors of solids formed, but they were mostly black and brown. However, occasionally at this point a maroon solid formed. When it was not confined, the maroon material exploded mildly. The black and brown product usually obtained turned completely black after sitting in the solution for a while even though sodium bisulfite was added to reduce the excess iodine. The black solid was removed from the solution and was dissolved in about 200 ml. of ether. The ether solution was extracted in a separatory funnel three times with a total of 500 ml. of 15 per cent sodium hydroxide and three times with a total of 500 ml. of water. These extractions removed much dark colored material. After the ether had evaporated, dark red crystals remained. These were dissolved in 50 ml. of 95 per cent ethanol and treated with carbon. Concentration and cooling the ethanol solution yielded yellow crystals, m. p. 80-81°C. This reaction was carried out many times; it was the best preparation of 2'-nitro-2-iodobiphenyl. Most of the yields were in the range of 25-30 per cent.

2'-Nitro-2-aminobiphenyl weighing 10.7 g. and 50 ml. of concentrated hydrochloric acid were put into a 500 ml. three-necked flask equipped with a heating mantle and mechanical stirrer. The mixture was heated at first, but all of the amine hydrochloride did not dissolve. The heating mantle was removed and the flask was surrounded by

an ice bath. After 10 g. of ice was added to the mixture, the temperature fell below 10°C. With stirring a solution of 3.0 g. of sodium nitrite in 10 ml. of water was added slowly and was allowed to react for a half hour. This solution was filtered to remove undissolved material, and then a solution of tetrafluoboric acid, 3.0 g. of boric acid dissolved in 10 g. of 48 per cent hydrofluoric acid, was added. During the addition the diazonium tetrafluoborate precipitated from the solution; it was filtered off and washed first with 50 ml. water, second with 50 ml. 95 per cent ethanol, and last with 50 ml. ether. After drying, the 2'-nitro-2-diazobiphenyl tetrafluoborate weighed 8.0 g. for a 71 per cent yield. The tetrafluoborate was added to a mixture of 40 g. of potassium iodide, 50 ml. of water, 50 ml. of hydrochloric acid, and 0.5 g. of 44F copper powder. This mixture stood for several hours while a reaction evidenced by slow bubbling took place. The mixture was washed with 30 ml. of ether and then the ether solution was extracted first with 15 per cent sodium hydroxide and then with water. After evaporation, the ether left dark red crystals. These were dissolved in 95 per cent ethanol and treated with decolorizing carbon. Upon concentration and cooling the ethanol solution, 2.2 g. of yellow crystals of 2'-nitro-2-iodobiphenyl were obtained for a 13.5 per cent yield.

In sulfuric acid and phosphoric acid.--About 20 g. of the red oil (see above, p. 35) and 200 ml. of concentrated sulfuric acid were added together in a one-liter three-necked flask equipped with a mechanical stirrer and surrounded with an ice-salt bath. After the solution had cooled below 5°C., a solution of 12 g. of sodium nitrite in 100 ml.

of sulfuric acid was added drop-wise with stirring to the solution. Next, 200 ml. of 85 per cent phosphoric acid was added. During the additions the temperature was kept below 10°C., but during the next hour of reaction the temperature rose to 21°C. with only a water bath for cooling instead of the ice bath. For the rest of the reaction lasting two hours the temperature rose to 27°C. without any bath. After this solution was poured into two liters of ice water, 15 g. of urea was added to destroy excess nitrous acid. Next, a solution of 30 g. of potassium iodide was added to the diazonium solution and a dark product formed atop the solution. After the reaction, this product was skimmed off and washed with sodium bisulfite solution. Attempts to recrystallize this product from benzene, cyclohexane, and 95 per cent ethanol were unsuccessful.

In acetic acid.--To 14 g. of 2'-nitro-2-aminobiphenyl in a one-liter flask equipped with a mechanical stirrer and cooled in an ice bath was added 10 ml. of concentrated sulfuric acid and 100 ml. of glacial acetic acid. The solution was cooled until the acetic acid solidified; then with stirring 5.0 g. of sodium nitrite was added with 200 ml. of cool glacial acetic acid. The mixture was let to react for three hours at a temperature just above the freezing point of the solution. When 20 g. of potassium iodide was washed into the flask with 300 ml. of cool glacial acetic acid, the solution darkened. After standing overnight, sodium thiosulfate solution was added to the acetic acid mixture until the solution stopped getting lighter in color. The solution was then extracted with approximately 100 ml. of benzene. Evaporation of the benzene left dark colored crystals. These crystals were dissolved

in 95 per cent ethanol and were treated with carbon. Upon cooling of the ethanol solution, 1.0 g. of 2'-nitro-2-iodobiphenyl, m. p. 81-82°C., was obtained. Further extraction of the water-acetic solution gave no more desired product. When this reaction was repeated using hydriodic acid instead of potassium iodide, no 2'-nitro-2-iodobiphenyl was obtained.

The Attempted Coupling Reactions of the 2'-Nitro-2-diazoniumbiphenyl Ion

The reaction of 2'-nitro-2-diazoniumbiphenyl ion with copper powder in water solution.--2'-Nitro-2-aminobiphenyl weighing 11 g., 35 ml. of concentrated hydrochloric acid, and about 100 g. of ice were added to a one-liter three-necked flask equipped with a mechanical stirrer and surrounded by an ice bath. After the solution had cooled to below -10°C., a solution of 7.0 g. of sodium nitrite in 25 ml. of water was added slowly with stirring and the solution was let to react for two hours. After undissolved material was filtered from the solution, 7.0 g. of 44F copper powder was added and the reaction was continued for four hours. The copper and other solids were filtered from the solution and were washed with hot 95 per cent ethanol and hot benzene. When these washes were combined and evaporated, they left black sticky crystals. This solid, after being dissolved in hot 95 per cent ethanol and being treated with carbon, gave a black tar on evaporation of the ethanol. Some of the black crystals were dissolved in a sodium hydroxide solution, and when hydrochloric acid was added, a black solid precipitated. This solid had a melting point of 125-127°C., and weighed less than 0.5 g.

The reaction of 2'-nitro-2-diazoniumbiphenyl ion with copper powder in acetic acid solution.--To a 500 ml. round-bottomed flask surrounded by an ice bath and equipped with a mechanical stirrer were added 11 g. of 2'-nitro-2-aminobiphenyl, 10 g. of concentrated sulfuric acid, and 150 ml. of glacial acetic acid. When the solution had cooled to 12°C., 3.5 g. of solid sodium nitrite was added slowly with stirring to the mixture. After the solution had reacted for an hour, 7.0 g. of 44F copper powder was added. The red color, possibly due to the diazonium ion, disappeared as the solution turned dark. The copper was let to react with the solution for one hour while the temperature rose to 30°C. The copper was filtered from the solution and was washed with hot 95 per cent ethanol forming a black solution. Upon evaporation, a dark black tar appeared. After redissolving the tar in 95 per cent ethanol and treating the solution with carbon, the ethanol solution yielded the tar again upon cooling. The acetic acid solution was placed on a steam bath which evaporated the acetic acid leaving a black tar. This tar was also dissolved in 95 per cent ethanol and treated with carbon, and, upon cooling the ethanol solution, yielded a black tar. No other purification was tried.

The Attempted Preparations of 2'-Nitro-2-bromobiphenyl and Related Reactions

The reduction of 2-nitrobromobenzene to 2-bromoaniline.--Into 50 ml. of benzene, which had been treated to remove thiophene, was dissolved 30 g. of 2-nitrobromobenzene. To this solution was added 0.50 g. of platinum oxide and the mixture was hydrogenated on a Parr pressure apparatus.

The uptake of hydrogen was in excess of three moles of hydrogen per mole of 2-nitrobromobenzene. After the spent catalyst had been filtered off, the solution was distilled under reduced pressure. When the benzene had been removed, a fraction which distilled between 100-115°C. at 15 mm. of mercury pressure was collected. This fraction froze near 24°C. and weighed 13 g. for a 51 per cent yield. A m. p. of 32°C. is listed for pure 2-bromoaniline (8).

The reduction of 2-nitrobromobenzene was tried with iron and hydrochloric acid, but the yield of 2-bromoaniline, which melted around 20°C., was less than that by the catalytic method.

The preparation of 2-bromoiodobenzene.--A 50 g. sample of the amine hydrochloride of 2-bromoaniline, 146 ml. of concentrated hydrochloric acid, 150 ml. of water, and 200 g. of ice were added to a one-liter flask equipped with a mechanical stirrer and surrounded by an ice bath. After the solution had cooled below 0°C., a solution of 24 g. of sodium nitrite in 120 ml. of water was added with stirring over a period of 25 minutes. The solution was permitted to react for an hour but was kept in the 0-3°C. range by the addition of ice. After filtering the undissolved material, a solution of 55 g. of potassium iodide in 55 ml. of water was added to the solution. The evolution of gases was apparent and a foamy liquid floated on top of the solution. After this mixture had been sitting for two hours, the liquid had settled to the bottom. This black liquid was separated from the solution, and was extracted with an approximately three per cent sodium bisulfite solution. This liquid was distilled under reduced pressure; a fraction which distilled between 100-120°C. at 15 mm. pressure was collected.

This liquid was dark colored, presumably due to the presence of free iodine; it weighed 45 g. for a per cent yield of 70.

The 2-bromoiodobenzene also was prepared from commercial 2-bromoaniline. In the process of the reaction the flask broke, but a per cent yield of 45 was obtained.

The reaction of 2-nitrobromobenzene and 2-iodobromobenzene with copper powder in dimethylformamide solution.--Into 200 ml. of dimethylformamide in a 500 ml. three-necked flask equipped with a heating mantle and mechanical stirrer were dissolved 15.5 g. of 2-iodobromobenzene and 12 g. of 2-nitrobromobenzene. After heating the solution to 80°C., 20 g. of treated 44F copper powder was added. The solution was allowed to react at 90-100°C. for two and a half hours. When the mixture had cooled, it was filtered from the copper, poured into two liters of water, and let stand overnight. From the water had appeared some crystals and a liquid. The crystals were recrystallized from ethanol to give needles, m. p. 124-125°C. (see above, p. 28). The liquid from the addition to water was dissolved in acetone and as the acetone evaporated yellow crystals, m. p. 115-120°C., appeared.

The reaction of 2-nitrobromobenzene and 2-iodobromobenzene in a mole to mole ratio with copper powder.--Into a 200 ml. round-bottomed flask heated by an electric mantle were placed 12 g. of 2-nitrobromobenzene and 17 g. of 2-iodobromobenzene. After the temperature had risen to 200°C., 20 g. of 44F copper powder was slowly added and the reaction was heated in the 240-260°C. range for one hour. The copper sludge was cooled and was washed with acetone. Upon evaporation of the acetone, there remained a black oil which was dissolved in 95 per cent ethanol.

When cooled, the ethanol solution first yielded dark oils but with further concentration and cooling yielded a yellow oil which crystallized. This small amount, less than 0.5 g., of yellow crystals had a m. p. of 50-55°C. The m. p. of the desired product, 2'-nitro-2-bromobiphenyl, is 66-67°C. (16).

The reaction of 2-nitrobromobenzene and 2-iodobromobenzene in a two to one molar ratio with copper powder.--2-Nitrobromobenzene weighing 20 g. and 2-iodobromobenzene weighing 14 g. were placed in a 200 ml. round-bottomed flask and heated to 240°C. by means of an electric mantle. At this point 15 g. of 44F copper powder was added slowly and the reaction was continued in the 240-250°C. range for one hour. After the mixture had cooled, it was washed with 300 ml. of acetone. The acetone solution was concentrated to 50 ml. and then, after diluting with 100 ml. of 95 per cent ethanol, was treated with decolorizing carbon. This solution was concentrated and yielded crystals on cooling. These were recrystallized in cyclohexane to give three to five g. of yellow crystals, m. p. 110-115°C. The alcohol-acetone solution was completely evaporated and there remained an oil which crystallized on standing to give about a gram of oily crystals, m. p. 55-65°C. These were likely 2'-nitro-2-bromobiphenyl because of similar melting points.

The reaction of 2-nitroiodobenzene and 2-iodobromobenzene with copper powder.--In a 200 ml. round-bottomed flask were placed 15 g. of 2-iodobenzene and 28 g. of 2-nitrobenzene; this was heated by means of a heating mantle to 240°C. To this solution 20 g. of 44F copper powder was added slowly and the mixture was let to react for one hour near the temperature of 250°C. After cooling, the mixture was washed with

acetone. The acetone was evaporated to less than 50 ml. and 100 ml. of 95 per cent ethanol was added. Concentration and cooling the ethanol solution yielded a black tar. The tar was washed with hot cyclohexane and, after evaporation and cooling the cyclohexane, yielded about 5.0 g. of yellow crystals, m. p. 110-115°C. No other solid was obtained from the tar.

Essentially this same procedure was repeated using 8.0 g. of 2-nitrochlorobenzene instead of the 2-nitroiodobenzene. The product was a black tar which could not be recrystallized from 95 per cent ethanol.

The attempted preparation of 2'-nitro-2-bromobiphenyl by the Sandmeyer reaction.--2'-Nitro-2-aminobiphenyl weighing 14 g., 5.0 ml. of sulfuric acid, and 100 g. of ice were added in a 500 ml. flask equipped with a mechanical stirrer and surrounded by an ice bath. To this mixture a solution of 5.0 g. of sodium nitrite in 20 ml. of water was added slowly with stirring. After letting the reaction proceed for an hour, freshly prepared cuprous bromide was added to the solution. On the addition of cuprous bromide a black mass appeared; this was filtered off after its formation had stopped. The black solid was placed in a Soxhlet and extracted with cyclohexane for 24 hours. The cyclohexane extract turned yellow, but upon complete evaporation it left nothing except a small amount of yellow tar.

The cuprous bromide was prepared by the following reactions. Copper sulfate weighing 16.5 g. and 17.6 g. of potassium bromide were added to 80 ml. of water and the resulting solution was warmed to about 60°C.; to this solution was added a solution of 7.2 g. of sodium bisulfite and 4.6 g. of sodium hydroxide in 40 ml. of water. As the

warming continued, cuprous bromide precipitated from the solution. The solution was then permitted to cool and the cuprous bromide was filtered off and was used at once.

The Preparations and Attempted Preparations of 2,2'-(2-Nitrophenyl)-biphenyl

In dimethylformamide.--Fourteen g. of 2'-nitro-2-iodobiphenyl were added to 80 ml. of dimethylformamide in a 500 ml. three-necked flask equipped with a condenser, mechanical stirrer, and a heating mantle. After the solution had heated to 120°C., 10 g. of partially treated 44F copper powder was added and the mixture was refluxed near 156°C. for three hours. At this time 10 g. more of the copper powder was added and the mixture was refluxed for three more hours. When the mixture had cooled somewhat, the copper sludge was filtered from the solution and the solution was poured into 600 ml. of water. After this water stood overnight, a residue had settled to the bottom. The water was decanted and the residue was washed with hot acetone. Upon concentration and cooling the acetone left a dark tar. This tar was dissolved in hot 95 per cent ethanol and was treated with carbon. After successive evaporations 8.5 g. of 2'-nitro-2-iodobiphenyl, m. p. 80-82°C., was obtained for a 61 per cent recovery of starting material. The last material which came from the ethanol solution was a small amount of yellow oil.

This reaction was repeated with the period of refluxing of the dimethylformamide solution being 96 hours. No solid product was obtained; only a yellow oil came from the ethanol solution.

At elevated pressure.--Five g. of 2'-nitro-2-iodobiphenyl, 25 ml. of dimethylformamide, and 5.0 g. of partially treated 44F copper powder were placed in a glass tube which was about 15 cm. long and four cm. in diameter. The tube was sealed, was placed in a high pressure apparatus, and was heated to the 210-222°C. range for 16 hours. After the copper sludge was filtered off, the solution was poured into 500 ml. of water which was permitted to stand overnight. A black residue appeared from the water and the water was decanted. The residue, except for the copper salts, dissolved in acetone. After the acetone had evaporated, an oily residue remained; this was extracted twice in a Soxhlet with 95 per cent ethanol. The first extract, after complete evaporation, gave a small amount of oily crystals which dissolved immediately in hot ethanol. The second ethanol extraction yielded after complete evaporation a red oil.

In nitrobenzene.--Three g. of 2'-nitro-2-iodobiphenyl and 25 ml. of nitrobenzene were added to 500 ml. flask equipped with a mechanical stirrer, a condenser, and a heating mantle. After 6.0 g. of partially treated 44F copper powder was added, the mixture was heated at reflux, which was near 204°C., for 1.5 hours. When the mixture had cooled somewhat, the copper sludge was filtered and washed with a few milliliters of nitrobenzene. Evaporation of the nitrobenzene on a steam bath left solid. This solid was dissolved in hot 95 per cent ethanol and treated with decolorizing carbon. Upon concentration and cooling, the ethanol solution yielded one g. of the starting compound, m. p. 81-82°C.; further cooling gave a 0.5 g. more of the same compound.

Without any solvent.--To a 200 ml. flask was added 11 g. of 2'-nitro-2-iodobiphenyl; this was heated to 200°C. with a heating mantle. At this time 5.0 g. of 44F copper powder was added with stirring. The reaction was kept at a temperature of 240-260°C. for a half hour. After cooling, the copper sludge was washed with acetone. Complete evaporation the acetone left a black tar; this was dissolved in hot 95 per cent ethanol and treated with decolorizing carbon. Upon cooling, the ethanolic solution yielded an oil. The supernatant liquid was decanted and on further evaporation and cooling yielded about three grams of the starting material, 2'-nitro-2-iodobiphenyl, m. p. 81-82°C. The oil, which was the first material to come from the ethanol solution, had crystallized somewhat. This crystalline oil was dissolved in hot 95 per cent ethanol; upon cooling, this solution yielded about 0.5 g. of yellow crystals, m. p. 157-160°C. A sodium fusion showed that the crystals contained nitrogen and no halogen.

This reaction was repeated several times with changes in procedure to yield for the most yellow crystals melting higher than 187°C. The best procedure for obtaining these crystals, labeled SDL V, and considered to be 2,2'-di(2-nitrophenyl)biphenyl, is given below.

Twenty-five g. of finely ground 2'-nitro-2-iodobiphenyl was mixed thoroughly with 25 g. of 44F copper powder. The mixture was placed in a six-inch test tube. The bottom of the test tube was immersed in a Wood's metal bath to the top of the mixture inside of the tube. The mixture was then heated between 220°C. and 230°C. for six hours. After cooling, the mixture was removed from the tubes and was extracted in a Soxhlet with acetone for four hours. Evaporation of

the acetone yielded two fractions of dark crystals and a considerable amount of black oil. The crystal fractions were extracted in a Soxhlet with 250 ml. portions of 95 per cent ethanol. The hot ethanol solution was decolorized with carbon and set aside to cool. Upon cooling, pale yellow crystals appeared. As long as the ethanol extracts of the dark solid yielded crystals, extraction with ethanol was continued. The crystals melting between 187.0-189.5°C. weighed 4.16 g., and those melting between 181-184°C. weighed 0.40 g.; this represents a 30 per cent yield of 2,2'-di(2-nitrophenyl)biphenyl. This reaction was tried several times; the best yield was 30 per cent with some of the others being around 15 per cent. The highest yields were obtained with a new sample of 44F copper powder. Analysis calculated for $C_{24}H_{16}N_2O_4$: carbon, 72.8; hydrogen, 4.03; and nitrogen, 7.08. Found: carbon, 72.1; hydrogen, 3.96; and nitrogen, 7.27.

The Preparations and Reactions Involved in the Proposed Preparation of 2,2'-Di(2-carboxyphenyl)biphenyl

The catalytic reduction of 2-nitroiodobenzene.--In a Parr low pressure apparatus were placed 45 g. of 2-nitroiodobenzene (see above p. 39), 150 ml. of 95 per cent ethanol, one ml. of acetic acid, and 0.4 g. of platinum oxide. The mixture was hydrogenated for three days until the calculated amount of hydrogen was consumed. During this period on two occasions 0.3 g. more of platinum oxide along with several drops of acetic acid were added because the uptake of hydrogen stopped twice. After filtering off the catalyst, the ethanol was boiled off the residue was steam distilled from a water solution made basic with sodium

hydroxide. Cooling of the distillate yielded white crystals, m. p. 47-49°C. The total amount of white crystals weighed 16 g. for a 38 per cent yield.

A sample of the water from which the white crystals were obtained was distilled and the distillate was acidified with dilute nitric acid. To this was added silver nitrate and yellow precipitate was formed. This indicates a deiodination reaction during the hydrogenation.

The chemical reduction of 2-nitroiodobenzene.--Stannous chloride dihydrate weighing 226 g., 200 ml. of concentrated hydrochloric acid, and 275 ml. of 95 per cent ethanol were added together in a three-liter flask and were stirred mechanically for about a half hour. Over a period of three hours 45 g. of 2-nitroiodobenzene was added slowly so as to maintain the temperature under 35°C. The reaction was stirred for seven additional hours after the addition and then it was allowed to stand overnight. The precipitate, which had formed overnight, was filtered from the solution and was washed first with 100 ml. of dilute sodium hydroxide and then with 100 ml. of 15 per cent sodium hydroxide. After water was added to the precipitate, it was steam distilled. The steam distillation was continued until no solid appeared in the distillate. The total distillate was cooled in a refrigerator overnight. The product, which consisted mainly of white crystals, was filtered from the water. The product, 2-iodoaniline, weighed 23 g. for a 62 per cent yield and had a m. p. of 47.5-49.5°C. Baeyer (2) reports the m. p. of this compound to be 51°C.

The attempted preparation of orthodiiodobenzene from orthophenylenediamine.--Twenty-two g. of ortho-phenylenediamine, 200 ml. of concentrated hydrochloric acid, and 200 g. of ice were added to a one-liter three-necked flask equipped with a mechanical stirrer and surrounded by an ice bath. When this mixture had cooled below -15°C., a solution of 28 g. of sodium nitrite in 40 ml. of water was added slowly with stirring. This solution was let to react for one hour during which the temperature rose to 3°C. After the solution was filtered from a little undissolved material, a solution of 64 g. of potassium iodide in 100 ml. of water was added. A dark solid appeared immediately and was filtered off after the reaction. In attempting to wash the iodine from the solid, the solid dissolved in 15 per cent sodium hydroxide. Upon acidification of a sample of the solution with hydrochloric acid a solid returned. The original solid did not melt at a room temperature of 30°C. Heilbron reports that 27°C. is the melting point of ortho-diiodobenzene (9). It was concluded that the product was not ortho-diiodobenzene.

The preparation of orthodiiodobenzene from 2-iodoaniline.--2-Iodoaniline (see above, p. 58) weighing 122 g. and 200 ml. of concentrated hydrochloric acid were mechanically stirred together in a one-liter three-necked flask for a half hour. At this time 200 g. of ice was added and the temperature fell below -10°C. A solution of 39 g. of sodium nitrite in 75 ml. of water was added over a period of an hour along with about 100 g. of ice. The temperature never rose above 3°C. during the addition the reaction mixture was let to stand for three hours and the temperature of the solution rose to 5°C. The solution

was filtered from undissolved solid, and when few milliliters of a solution of 85 g. of potassium iodide in 200 ml. of water was added to the dizaonium solution, a violent reaction occurred. Ice was added to the diazonium solution and the potassium iodide solution was diluted to 400 ml. With stirring the potassium iodide solution was added to the diazonium solution. The reaction appeared to be rapid at first and cooling by the addition of ice was necessary; however as the addition of potassium iodide solution was continued, the reaction slowed somewhat. After the reaction stood for three hours, a liquid had settled from the solution. The water was decolorized with sodium bisulfate and was decanted from the heavier purple liquid. The liquid was washed with sodium hydroxide solution and then dried overnight with calcium chloride. It was distilled under reduced pressure from 120-145°C. at 6.5 mm. This material was redistilled and the fraction from 130-145°C. at 9.5 mm. was collected. The product, ortho-diiodobenzene, was still purple in color and weighed 92.6 g. for a 51 per cent yield.

The reaction of ortho-diiodobenzene and methyl 2-iodobenzoate with copper powder.--Twenty g. of ortho-diiodobenzene was heated to reflux which was near 260°C. At this time a few drops of methyl 2-iodobenzoate and some 44F copper powder were added slowly. This addition was continued for a half hour until 8.0 g. of methyl 2-iodobenzoate and 6.0 g. of the copper were used. This mixture was heated at 290-305°C. for one hour. After the mixture had cooled, it was extracted with acetone in a Soxhlet for several hours. The acetone was evaporated and the residue was distilled under a reduced pressure of 1.5 mm. Four fractions were obtained: the first, 1.5 ml. collected between 45-75°C.; the second,

2.5 ml. collected between 75-100°C.; the third, 0.75 ml. collected between 100-125°C.; and the fourth, 2.5 ml. collected between 125-139°C. Fraction four was dissolved in 15 ml. of 95 per cent ethanol and 3.0 g. of potassium hydroxide in 10 ml. of water was added. This solution was refluxed for three hours and was permitted to stand overnight. A little solid was filtered from the solution; water was added and a red oil appeared. After the solution was removed from the oil, the solution was diluted further with water and was extracted with ether. Evaporation of the ether left a yellow-red tar which was discarded. The water solution was warmed to expel the ether and was acidified with acetic acid to a pH of seven, as shown by hydrion paper. At this pH the solution yielded a red oil which was discarded. The solution was acidified with excess acetic acid and yellow oily crystals came from the solution. Continued acidification with hydrochloric acid yielded white crystals, diphenic acid (24). The yellow oily crystals were recrystallized from concentrated acetic acid which yielded yellow crystals, m. p. 147.5-149.5°C. These weighed 0.75 g. and were a 7.3 per cent yield of 2'-carboxy-2-iodobiphenyl (24).

This reaction was tried several times with variations in quantities of reactants and conditions; sometimes no 2-carboxy-2-iodobiphenyl was obtained, but in no case was the yield better than that mentioned above.

The Preparation and Attempts of Preparation of 2,2'-Di(2-aminophenyl) biphenyl

<u>The reduction in benzene solution.</u>--Forty ml. of thiophene free benzene

dissolved 0.85 g. of 2,2'-di(2-nitrophenyl)biphenyl. To this solution was added 0.03 g. of platinum oxide, and the mixture was hydrogenated using a Parr low pressure apparatus. The reaction did not take up the calculated amount of hydrogen. After the catalyst was filtered from the reaction solution, the benzene was evaporated and a yellow oil remained. This oil was dissolved in hot ethanol, and upon cooling yielded the starting material as light yellow crystals, m. p. 185.5-186.5°C. Complete evaporation of the ethanol solution left a dark red oil. The oil was washed with hot concentrated hydrochloric acid, and, after cooling, this solution was neutralized with ammonium hydroxide. A tan solid of undiscernable melting point was formed. This solid was dissolved in dilute hydrochloric acid and ice and sodium nitrite were added to the solution. Addition of beta-naphthol in sodium hydroxide gave a red precipitate indicating the presence of an aromatic amine.

This reaction was repeated. Forty ml. of benzene solution containing 0.367 g. of 2,2'-di(2-nitrophenyl)biphenyl was let to stand in contact with Raney nickel. After the Raney nickel was filtered off, 0.5 g. of platinum oxide was added and the solution was hydrogenated on a Parr low pressure apparatus. The uptake of hydrogen was about only 90 per cent complete even though 0.2 g. of additional platinum oxide was added. After the catalyst was filtered off and the benzene was evaporated, a red oil remained. A portion of this oil was dissolved in 95 per cent ethanol and cooled, but the oil reappeared. The other portion of the oil was washed with 6 N hydrochloric acid. When this acid solution was neutralized with ammonium hydroxide, a white solid appeared. This solid gave a positive beta-naphthol test and gave

an indefinite melting point near 66-70°C. This material was labeled SDL VI and was suspected of being at least in part 2,2'-di(2-aminophenyl)-biphenyl.

The reduction in dioxane solution.--A possibility of using another solvent for the hydrogenation of 2,2'-di(2-nitrophenyl)biphenyl was investigated. Since the compound was found to be insoluble in cyclohexane but soluble in dioxane, the latter offered the possibility of serving as a solvent. Accordingly, 3.092 g. of 2,2'-di(2-nitrophenyl)-biphenyl was dissolved in 30 ml. of dioxane. After 0.5 g. of platinum oxide was added the mixture was hydrogenated on the Parr apparatus. The reaction stopped several times, four separate additions of 0.2 g. of catalyst were from time to time continued until the reaction was 99 per cent complete as indicated by the uptake of hydrogen. After removal of the catalyst and evaporation of the dioxane, the red oil remaining had the same properties as the red oil in the previous section. A sample of this red oil was dissolved in dilute hydrochloric acid. Addition of ammonium hydroxide to the acid solution produced a white solid with an indefinite melting point near 65-70°C. The white solid was washed with benzene and left a white residue which gave a positive test for chloride and ammonium ions and which evaporated on ignition. The benzene wash was evaporated and a dark red oil was left. This oil was vacuum sublimed to give a white solid, m. p. 132-136°C. This white gave a positive Tollen's test, which indicated that the material was not completely reduced. Some of this material, weighing 1.175 g., was dissolved in 95 per cent ethanol and was hydrogenated on the Parr apparatus with platinum oxide catalyst. The material absorbed 0.0096 moles

of hydrogen per 0.0035 moles of assumed 2,2'-di(2-aminophenyl)biphenyl. The ethanol solution on evaporation and cooling gave white crystals, m. p. 140.0-141.5°C., and further evaporation and cooling gave a white solid, m. p. 136-138°C.

Once, however, the dioxane solution from the reduction was diluted with water and upon standing yielded pink-white crystals. This crystallization could not be repeated in other runs. The solid had a m. p. of 138-142°C. and gave a positive beta-naphthol test. A sample of these crystals was vacuum sublimed between 140-150°C. at 10 mm. to give a white solid, m. p. 138.0-139.5°C. The analysis of nitrogen in this solid agreed with the per cent nitrogen in 2,2'-di(2-aminophenyl)-biphenyl: 8.33 (calc.), 8.20 (found).

The reduction in 95 per cent ethanol.--2,2'-Di(2-nitrophenyl)biphenyl weighing 1.128 g. was added to 100 ml. of 95 per cent ethanol; the solid dissolved to a small extent. To this mixture was added 0.2 g. of platinum oxide and the mixture was hydrogenated on the Parr apparatus. The hydrogenation, which used a little more hydrogen than the calculated amount, took about three hours. This was much less time than when benzene or dioxane was used as the hydrogenation solvent. After the catalyst was filtered off, the ethanol solution was concentrated and cooled. This solution yielded 0.220 g. of white crystals, m. p. 140-141°C., and a second crop, m. p. 130-135°C., weighing 0.256 g. This total weight is a per cent yield of 49.7. This was the best preparation of 2,2'-di(2-aminophenyl)biphenyl.

The Diazotization and Sandmeyer Reactions of 2,2'-Di(2-aminophenyl)-biphenyl

Impure 2,2'-di(2-aminophenyl)biphenyl.--A small sample, approximately 0.1 g. of SDL VI, m. p. 60-70°C., was dissolved in 15 ml. of dilute hydrochloric acid and was cooled in an ice bath. When the temperature of the solution was near 0°C., a solution of sodium nitrite in water was added. The solution was let to react for a half hour and at that time the solution gave a positive starch-iodide test. To this solution was added a solution of approximately one g. of potassium iodide in five ml. of water; a brown foamy solid appeared. This solid was filtered from the solution and was dissolved in ether. The ether was extracted with 15 per cent sodium hydroxide and then was allowed to evaporate. A brown tar left by the evaporation of the ether was dissolved in 95 per cent ethanol and was treated with charcoal. Upon evaporation there remained a brown solid with an indistinct melting point. A sodium fusion on the solid gave a positive test for iodine and a negative test for nitrogen. This product was labeled SDL VII and was suspected of containing 2,2'-di(2-iodophenyl)biphenyl.

Using a purer sample of 2,2'-di(2-aminophenyl)biphenyl.--A sample of 2,2'-di(2-aminophenyl)biphenyl weighing 0.246 g. was dissolved in 20 ml. of 4 N hydrochloric acid solution. After cooling this solution with ice, it was added to a solution of 0.12 g. of sodium nitrite in 10 ml. of ice water. When this solution had reacted for 20 minutes, it was poured into a solution of one g. of potassium iodide in 10 ml. of water. A brown solid formed and the reaction was permitted to continue for three hours. After the brown solid was filtered off, it

was dissolved for the most part in ether. The small amount of ether insoluble material melted above 250°C., contained no halogen or nitrogen, and burned completely on ignition. The ether solution was washed with 10 per cent sodium hydroxide and with water. When the ether evaporated, a brown tar remained. The tar was dissolved in 95 per cent ethanol and treated with charcoal. Upon evaporation of the ethanol, a brown solid formed. This solid was vacuum sublimed between 140-160°C. and at 2.0 mm. pressure. This yielded 56 mg. of a yellow solid, m. p. 109.0-110.5°C. The analysis of iodine in the solid did not agree with per cent iodine in 2,2'-di(2-iodophenyl)biphenyl: 45.5 (calc.), 25.0 (found). No other diazotization and Sandmeyer reactions of 2,2'-di(2-aminophenyl)biphenyl gave a product melting near 109.0-110.5°C.

This reaction was repeated using 2,2'-di(2-aminophenyl)biphenyl, m. p. 138-140°C., obtained from the reduction in ethanol solution. The vacuum sublimation of the product yielded again a yellow solid, m. p. 65-70°C. This solid was recrystallized from 95 per cent ethanol to give white crystals, m. p. 145.0-146.5°C. Further concentration gave a lower melting material. A sample of the highest melting material was crystallized again from 95 per cent ethanol and white crystals, m. p. 147.5-149.0°C. were obtained. Analysis calculated for $C_{24}H_{17}I$: carbon, 66.6; hydrogen, 3.94; and iodine, 29.4. Found: carbon, 66.34; hydrogen, 3.60; and iodine, 30.18.

The Reaction of Impure 2'-Phenyl-2-(2-iodophenyl)biphenyl with Copper Powder

A sample of impure 2'-phenyl-2-(2-iodophenyl)biphenyl, SDL VII, weighing 226 mg. and melting at 65-70°C. (see above, p. 65) and 0.5 g.

of 44F copper powder in a test tube were heated near 250°C. for five hours by means of a Wood's metal bath. A small amount of white material condensed in the upper part of the tube; this material was vacuum sublimed at 250°C. and 2.0 mm. pressure to give a small amount, estimated to be around 10 mg., of white solid melting between 190-215°C. Most of the solid was used in attempting a sodium fusion, which gave a negative test for halogens. The copper sludge from the initial reaction was washed with chloroform, and upon complete evaporation, the chloroform left a yellow solid, which melted indistinctly between 80-120°C.

A reaction similar to the one in the last paragraph was tried. A 40 mg. sample of impure 2'-phenyl-2-(2-iodophenyl)biphenyl, m. p. 109.0-110.5°C. and 0.2 g. of 44F copper powder were placed in a three in. test tube. Into this test tube was placed a hypodermic needle through which flowed a stream of nitrogen. The test tube was heated in a Wood's metal bath between 220-230°C. for five hours. White crystals formed on the needle and on the sides of the tube. These white crystals which were scraped from the needle weighed less than five mg. and had a m. p. of 204-207°C., which was determined microscopically. The crystals gave a negative Beilstein's test for halogens. This material was labeled SDL VIII, and the remaining amount was used preparing an infrared spectrum (see below, p. 72). The reaction copper was washed with chloroform which upon evaporation left a yellow solid melting below 130°C.

CHAPTER IV

CONCLUSIONS

Tetraphenylene may yet be synthesized by Ullmann reactions, but only after a series of difficult reactions.

2,2'-Di(2-nitrophenyl)biphenyl, 2,2'-di(2-aminophenyl)biphenyl, and 2'-phenyl-2-(2-iodophenyl)biphenyl, heretofore unknown compounds, were synthesized. If 2,2'-di(2-iodophenyl)biphenyl could be prepared from 2,2'-di(2-aminophenyl)biphenyl, perhaps this approach could still be used to prepare tetraphenylene.

The procedure of preparing 2'-nitro-2-aminobiphenyl was clarified.

The chemistry of the 2'-nitro-2-diazoniumbiphenyl ion is complex and perhaps should be studied further.

Unsymmetrical Ullmann reactions are a poor approach to the tetraphenyl system because they are usually of low yield.

APPENDIX

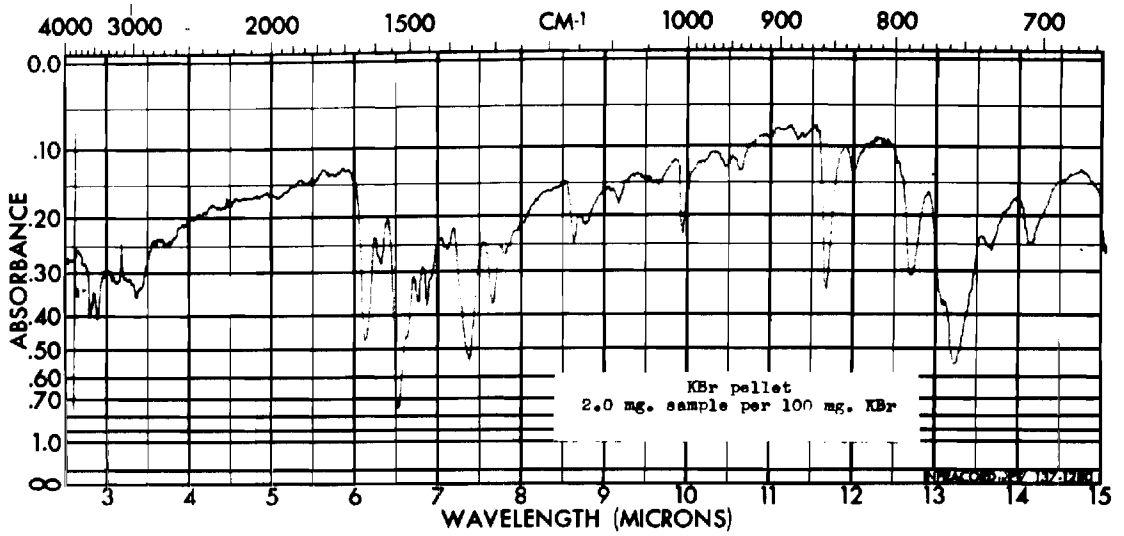

Figure 19. The Infrared Spectrum of 2'-Nitro-2-aminobiphenyl

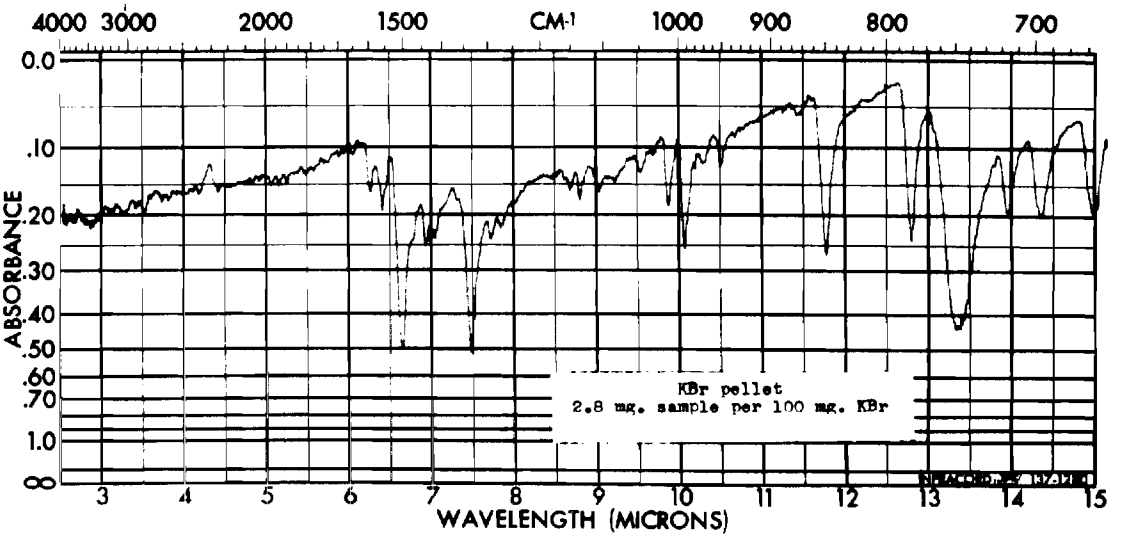

Figure 20. The Infrared Spectrum of 2'-Nitro-2-iodobiphenyl

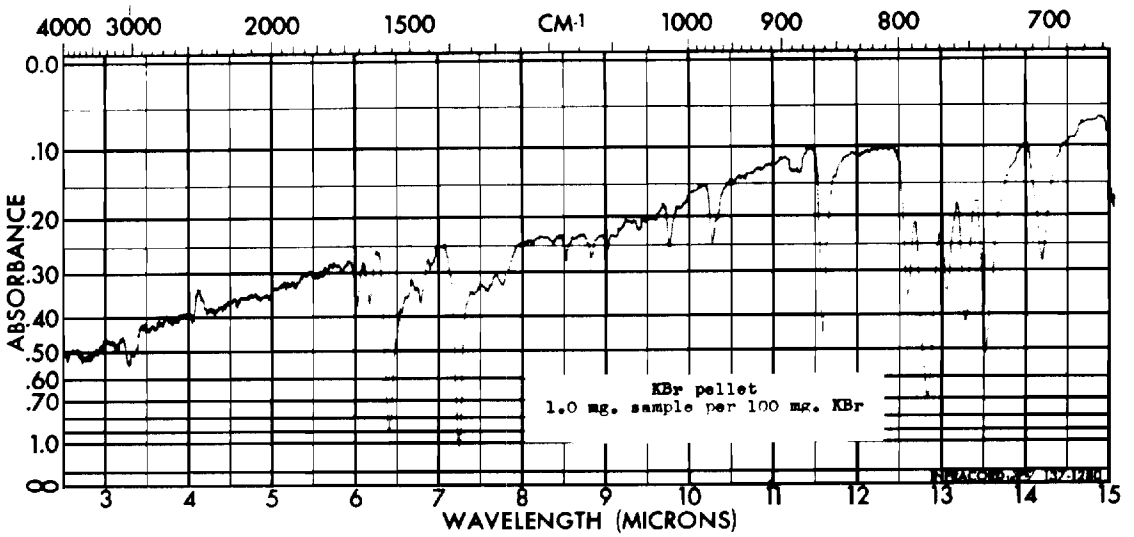

Figure 21. The Infrared Spectrum of 2,2'-Di(2-nitrophenyl)biphenyl

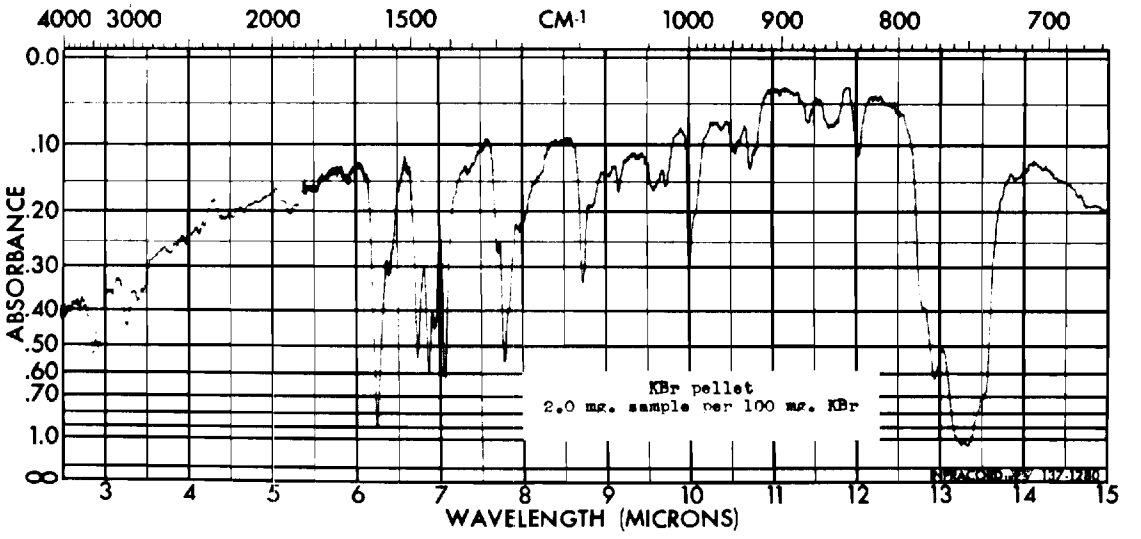

Figure 22. The Infrared Spectrum of 2,2'-Di(2-aminophenyl)biphenyl

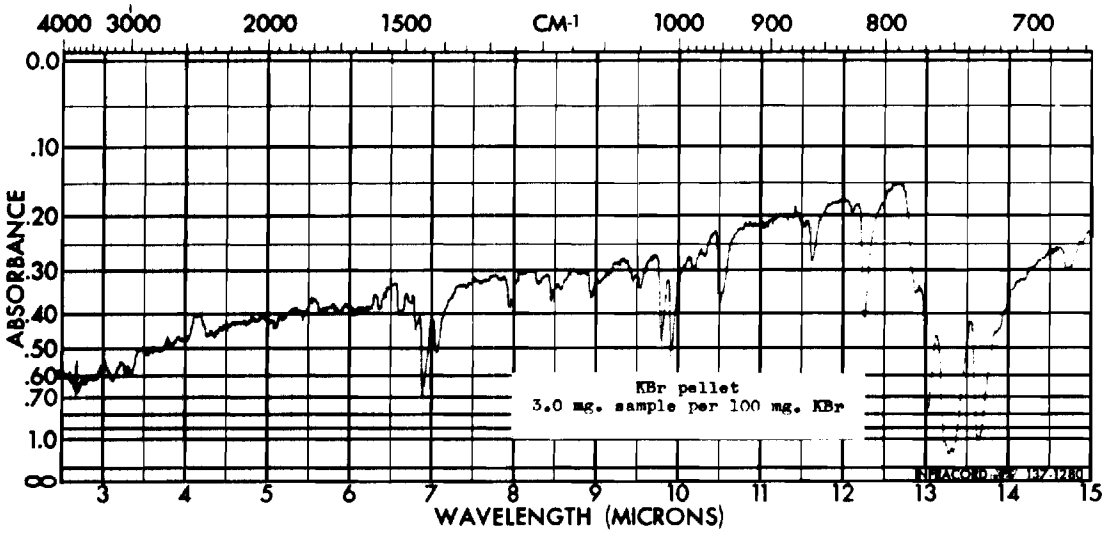

Figure 23. The Infrared Spectrum of 2'-Phenyl-2-(2-iodophenyl)biphenyl

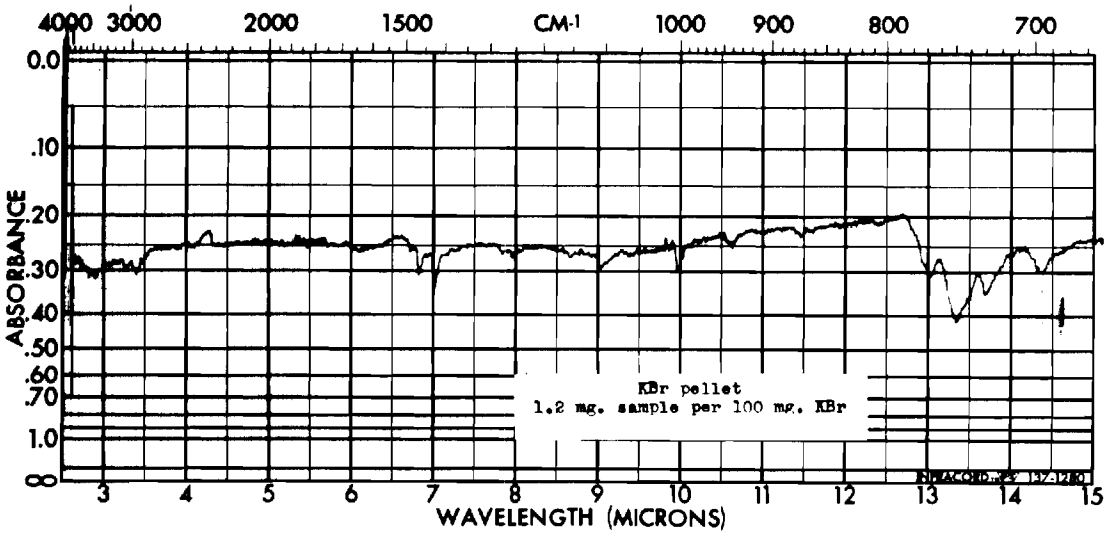

Figure 24. The Infrared Spectrum of SDL VIII

BIBLIOGRAPHY

1. Angeletti, A., Gazzetta chimica italiana, 61, 832 (1931); Chemical Abstracts, 26, 1919 (1932).

2. Baeyer, A., Berichte der deutschen chemischen Gesellschaft, 38, 2760 (1905).

3. Clarke, H. T. and Taylor, E. R., Organic Syntheses, A. H. Blatt, (ed.), New York, John Wiley & Sons, Inc., 1943, Collective Volume II, p. 135.

4. Courtot, C., Nicolas, L., and Liang, T. H., Comptes rendus des Seances de l'Acadamie des Seances, 186, 1624 (1928).

5. Fairfull, A. E. S., Peak, D. A., Short, W. F., and Watkins, T. I., Journal of the Chemical Society, (London), 1952, 4700.

6. Fanta, P. E., Chemical Reviews, 38, 139 (1946).

7. Fuson, R. C. and Cleveland, E. A., Organic Syntheses, Horning, E. C. (ed.), New York, John Wiley & Sons, Inc., 1955, Collective Volume III, p. 339.

8. Heilbron, I. M. (ed.), Dictionary of Organic Compounds, New York Oxford University Press, 1943, Volume I, p. 270.

9. Ibid., p. 865.

10. Karle, I. L. and Brockway, L. O., Journal of the American Chemical Society, 66, 1974 (1944).

11. Kleiderer, E. C. and Adams, R., Journal of the American Chemical Society, 55, 4225 (1933).

12. Kornblum, N. and Kendall, D. L., Journal of the American Chemical Society, 74, 5782 (1952).

13. Kuhn, R., Justus Liebigs Annalen der Chemie, 475, 131 (1929).

14. Le Fevre, R. J. W. and Vine, H., Journal of the Chemical Society, (London), 1929, 733.

15. Lothrop, W. C., Journal of the American Chemical Society, 63, 1187 (1941).

16. Mascarelli, L., Gatti, D., and Pirona, M., Gazzetta chimica italiana, 61, 782 (1931); Chemical Abstracts, 26, 1591 (1932).

17. Mascarelli, L., Gatti, D., and Pirona, M., Atti della Accademia dei Lincei, 14, 506 (1932); Chemical Abstracts, 26, 4322 (1932).

18. Niementowski, St. V., Berichte der deutschen chemischen Gesellschaft, 34, 3325 (1901).

19. Purdie, D., Journal of the American Chemical Society, 63, 2277 (1941).

20. Rapson, W. S., Shuttleworth, R. G., and van Niekert, J. N., Journal of the Chemical Society, (London), 1943, 327.

21. Sadler, A. M. and Powell, G., Journal of the American Chemical Society, 56, 2650 (1934).

22. Shoesmith, J. B. and Slater, R. H., Journal of the Chemical Society, (London), 125, 2278 (1924).

23. Shuttleworth, R. G., Rapson, W. S., and Stewart, E. T., Journal of the Chemical Society, (London), 1944, 71.

24. Sicar, A. C. and Majumdar, J. N., Journal of the Indian Chemical Society, 5, 417 (1928).

25. Ullmann, F. and Dieterle, P., Berichte der deutschen chemischen Gesellschaft, 37, 24 (1904).

26. Vogel, A. I., A Text Book of Practical Organic Chemistry, New York, Longmans, Green Co., 1954, p. 168.

VITA

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